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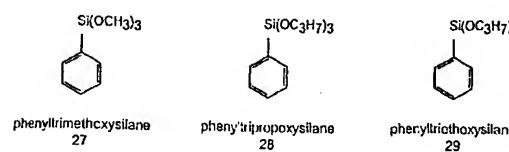
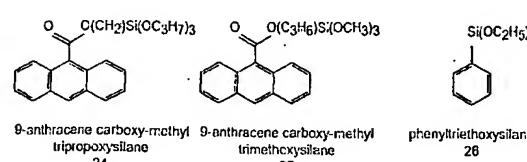
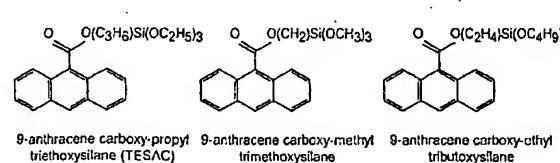
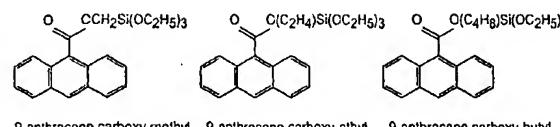
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(54) Title: ANTI-REFLECTIVE COATINGS FOR PHOTOLITHOGRAPHY AND METHODS OF PREPARATION THEREOF



(57) Abstract: Anti-reflective coating materials for ultraviolet photolithography include at least one absorbing compound and at least one material modification agent, such as at least one porogen, at least one high-boiling solvent, at least one densifying agent, at least one capping agent, at least one leveling agent, at least one catalyst, at least one replacement solvent, at least one pH tuning agent, and/or a combination thereof that are incorporated into inorganic-based materials or inorganic compositions and/or compounds. Suitable absorbing compounds are those that absorb around wavelengths such as 365 nm, 248 nm, 193 nm and 157 nm that may be used in photolithography.

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**ANTI-REFLECTIVE COATINGS FOR PHOTOLITHOGRAPHY AND
METHODS OF PREPARATION THEREOF**

FIELD OF THE INVENTION

5 The present invention relates generally to anti-reflective coating materials and more specifically to anti-reflective layers for use in photolithography and methods of producing the materials.

BACKGROUND OF THE INVENTION

10 To meet the requirements for faster performance, the characteristic dimensions of features of integrated circuit devices have continued to be decreased. Manufacturing of devices with smaller feature sizes introduces new challenges in many of the processes conventionally used in semiconductor fabrication. One of the most important of these fabrication processes is photolithography.

15 It has long been recognized that linewidth variations in patterns produced by photolithography can result from optical interference from light reflecting off an underlying layer on a semiconductor wafer. Variations in photoresist thickness due to the topography of the underlying layer also induce linewidth variations. Anti-reflective coatings (ARC) applied under a photoresist layer have been used to prevent interference from reflection of the 20 irradiating beam. In addition, anti-reflective coatings partially planarize the wafer topography, helping to improve linewidth variation over steps because the photoresist thickness is more uniform.

25 Organic polymer films, particularly those that absorb at the i-line (365 nm) and g-line (436 nm) wavelengths conventionally used to expose photoresists, and at the recently used 157 nm, 193 nm, 248 nm wavelengths, have been employed or are being tested as anti-reflective coatings. However, the fact that the organic ARC's share many chemical properties with the organic photoresists can limit usable process sequences. Furthermore, ARC's, including both organic and inorganic ARC's, may intermix with photoresist layers. Organic

and inorganic ARC's can mix with photoresist layers if they are not sufficiently baked or cured.

One solution to avoid intermixing is to introduce thermosetting binders as additional components of organic ARC's, as described for example in U.S. Patent No. 5,693,691 to Flaim et al. Dyes may also be incorporated in organic ARC's, as well as, optionally, additional additives such as wetting agents, adhesions promoters, preservatives, and plasticizers, as described in U. S. Patent No. 4,910,122 to Arnold et al. Another attempt to avoid intermixing is found in US Patent 6,268,108 issued to Iguchi et al. However, the compositions for forming antireflective coatings found in Iguchi must be irradiated with actinic rays in order to produce an acid, which in turn activates a crosslinking reaction. Even though these previous patents may address some of the issues with intermixing, the problem of the lack of 86- to 90-degree uniformity on the resist edges because of the coupled ARC layer has not been addressed in the prior art.

Photoresists and anti-reflective coatings can also influence one another to the extent that the chemical properties of the anti-reflective coating and/or the resist material can lead the resist to "fall over" once a pattern has been developed into the resist. In other words, the patterned resist sidewall can't maintain an approximate 90-degree angle with respect to the anti-reflective coating after photoresist developing. Instead the resist will take on a 120-degree or an 80-degree angle with respect to the anti-reflective coating. These imperfections are also an indication that photoresist materials and anti-reflective coatings are not necessarily chemically, physically or mechanically compatible.

Photoresists and anti-reflective coatings can also have substandard or unacceptable etch selectivity or stripping selectivity. Poor etch selectivity and/or stripping selectivity can lead to low etch rates for the film. Poor etch selectivity can also lead to poor transfer of critical dimensions from the printing step(s) through the etch step(s). Attempts have been made at improving the etch rate by providing highly absorbing substances with substitution groups that can condense the silane compound to specific silane compounds, as seen in JP Patent Application No.: 2001-92122 published on April 6, 2001. However, the etch selectivity obtained with these reactive compounds are not sufficient for most photoresists and anti-reflective coatings and require additional chemical reaction steps that may not be necessary.

In addition, photoresists and anti-reflective coatings often have difficulty with fill bias and voiding in via structures to the point where any planarization of the surface is severely compromised. Oftentimes, the two goals of increasing etch selectivity and minimizing fill bias and voiding directly conflict with one another, which is why it's important to review and 5 understand the goals of each group of applications. Also, to sufficiently fill and planarize via arrays requires that a relatively thick anti-reflective coating exist. If the ARC coating is organic, such a thick coating will further compromise the accurate transfer of the as patterned critical dimension through the film stack.

A class of materials that can be used as an anti-reflective layer is spin-on-glass (SOG) 10 compositions containing a dye. Yau et al., U.S. Patent No. 4,587,138, disclose a dye such as basic yellow #11 mixed with a spin-on-glass in an amount approximately 1% by weight. Allman et al. U. S. Patent No. 5,100,503 disclose a cross-linked polyorganosiloxane containing an inorganic dye such as TiO₂, Cr₂O₇, MoO₄, MnO₄, or ScO₄, and an adhesion promoter. Allman additionally teaches that the spin-on-glass compositions also serve as a 15 planarizing layer. However, the spin-on-glass, dye combinations that have been disclosed to date are not optimal for exposure to the deep ultraviolet, particularly 248 and 193 nm, light sources that are coming into use to produce devices with small feature sizes. Furthermore, not all dyes can be readily incorporated into an arbitrary spin-on-glass composition. Also, even though these ARC's are chemically different than the previously mentioned organic 20 ARC's, the coupled resist layers can still suffer from "falling over" after being developed, as based on the chemical, physical, and mechanical incompatibility of the ARC layer and the resist layer – which is a common problem when trying to couple resist materials and anti-reflective coatings.

In developing anti-reflective coatings that can a) absorb strongly and uniformly in the 25 ultraviolet spectral region; b) keep the resist material from "falling over" and expanding outside or contracting inside of the intended resist line and c) be impervious to photoresist developers and methods of production of spin-on glass anti-reflective coatings, Baldwin et al developed several anti-reflective coatings that are superior to conventional anti-reflective coatings, including those materials and coatings found in US Issued Patents 6,268,457 issued 30 on July 31, 2001; 6,365,765 issued on April 2, 2002; 6,368,400 issued on April 9, 2002; US Patent Applications Serial Nos: 09/491166 filed January 26, 2000; 10/012651 filed November 5, 2001; 10/012649 filed November 5, 2001; 10/001143 filed November 15, 2001;

PCT Applications Serial Nos: PCT/US00/15772 filed on June 8, 2000; WO 02/06402 filed on July 12, 2001; PCT/US01/45306 filed on November 15, 2001; Pending PCT Application filed on October 31, 2002 (Serial No. not yet assigned); European Patent Applications Serial No. 00941275.0 filed on June 6, 2000; and 01958953.0 filed on July 17, 2001, which are all 5 commonly assigned and incorporated herein by reference in their entirety. Honeywell Electronic Materials™ also produces ACCUSPIN® 720 that is a spin-on polymer which comprises a low dielectric constant methylphenylsilsesquioxane compound. The organic content of this product is approximately 47% and is formulated in a high flashpoint solvent, such as n-propoxypropanol. Its "n" and "k" properties at 193 nm wavelength are 10 approximately 1.9 and 0.6 respectively. However, with all of these materials, it would be beneficial to be able to modify the materials, coatings and films described therein to improve etch selectivity and/or stripping selectivity and to minimize fill bias.

Certain applications, such as tri-level photoresist schemes, in the Integrated Circuits (IC) industry require that a spin-on silicate film be used as a sacrificial hardmask. In 15 photolithography with chemically amplified resists, a certain degree of film density is a requirement of the substrate film, such as a UV absorbing organosiloxane film, to inhibit the diffusion of acid from the resist into itself. The loss of acid through diffusion into the underlying film leads to resist footing. Interface mismatch can also lead to problems, such as resist collapse. Thermal budgets limit how dense the silicate or siloxane-based films can be 20 made through thermal processing. For the tri-layer resist process, the denser the silicate film, the better the pattern transfer through the underlying films.

Therefore, an absorbing anti-reflective coating and lithography material that a) absorbs strongly and uniformly in the ultraviolet spectral region, b) can keep the resist material from "falling over" and expanding outside or contracting inside of the intended resist 25 line, c) would be impervious to photoresist developers and methods of production of the SOG anti-reflective coating described; d) can satisfy any goals of increasing etch selectivity and/or stripping selectivity, e) can satisfy any goals of minimizing fill bias and voiding in via structures, and f) can satisfy goals directed to densifying the film or layer would be desirable to advance the production of layered materials, electronic components and semiconductor 30 components.

SUMMARY OF THE INVENTION

An anti-reflective coating material for ultraviolet photolithography comprises at least one inorganic-based compound; at least one absorbing compound and at least one material modification agent. The at least one material modification agent may comprise at least one 5 porogen, at least one high-boiling solvent, at least one catalyst, at least one leveling agent, at least one densifying agent, at least one pH tuning agent, at least one replacement solvent, at least one capping agent, at least one adhesion promoter, such as a resin-based material and/or a combination thereof that are incorporated into the inorganic-based material or compound.

A method of making an absorbing anti-reflective composition includes combining at 10 least one inorganic-based composition, at least one incorporatable absorbing compound, and at least one material modification agent that may comprise at least one porogen, at least one high-boiling solvent, at least one leveling agent, at least one catalyst, at least one densifying agent, at least one pH tuning agent, at least one capping agent, at least one adhesion promoter and/or at least one replacement solvent, an acid/water mixture, such as a nitric acid/water 15 mixture, and at least one solvent to form a reaction mixture.

In another method of making an absorbing anti-reflective composition, at least one inorganic-based composition or inorganic material, at least one incorporatable absorbing compound, at least one material modification agent, such as at least one porogen, at least one high-boiling solvent, at least one catalyst, at least one densifying agent, at least one pH tuning 20 agent, at least one leveling agent, at least one capping agent, at least one replacement solvent, at least one adhesion promoter and/or a combination thereof, and at least one additional solvent can be combined to form a reaction mixture.

In yet another aspect of the subject matter disclosed, an absorbing anti-reflective composition is produced comprising at least one silicon-based compound, at least one 25 incorporatable absorbing compound that absorbs light at wavelengths less than about 375 nm, and at least one material modification agent, such as at least one porogen, at least one high-boiling solvent, at least one capping agent, at least one catalyst, at least one leveling agent, at least one densifying agent, at least one pH tuning agent, at least one adhesion promoter and/or at least one replacement solvent.

BRIEF DESCRIPTION OF THE FIGURES

Figs. 1a – 1f show the chemical formulas of absorbing compounds incorporated into inorganic-based compositions and materials.

5 Figs. 2a-2h illustrate the use of absorbing anti-reflective compositions in a photolithography process.

Fig. 3 graphically illustrates MW (daltons) v. days at about 40°C for a contemplated compound.

Fig. 4 graphically illustrates MW (daltons) v. days at about 40°C for a contemplated compound.

10 Fig. 5 graphically illustrates MW (daltons) v. days at about 40°C for a contemplated compound.

Fig. 6 graphically illustrates Thickness (Angstroms) v. days at about 40°C for a contemplated compound.

15 Fig. 7 graphically illustrates Thickness (Angstroms) v. days at about 40°C for a contemplated compound.

Fig. 8 graphically illustrates Thickness (Angstroms) v. days at about 40°C for a contemplated compound.

Fig. 9 graphically illustrates Polydispersity (Mw/Mn - unitless) v. days at about 40°C for a contemplated compound.

20 Fig. 10 graphically illustrates Polydispersity (Mw/Mn - unitless) v. days at about 40°C for a contemplated compound.

Fig. 11 graphically illustrates Polydispersity (Mw/Mn - unitless) v. days at about 40°C for a contemplated compound.

25 Fig. 12 graphically illustrates pH (unitless) v. days at about 40°C for a contemplated compound.

Fig. 13 graphically illustrates pH (unitless) v. days at about 40°C for a contemplated compound.

Fig. 14 graphically illustrates pH (unitless) v. days at about 40°C for a contemplated compound.

Fig. 15 graphically illustrates Temperature (°C) v. Time (minutes) for a group of contemplated compounds.

5 Fig. 16 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

Fig. 17 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

10 Fig. 18 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

Fig. 19 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

Fig. 20 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

15 Fig. 21 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

Fig. 22 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound and also shows SEM data for one contemplated embodiment.

20 Fig. 23 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound and also shows SEM data for one contemplated embodiment.

Fig. 24 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound and also shows SEM data for one contemplated embodiment.

25 Fig. 25 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound.

Fig. 26 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound and also shows SEM data for one contemplated embodiment.

Fig. 27 graphically illustrates % Fill (Thickness over via/via depth) v. blanket film thickness (Angstroms) for a contemplated compound and also shows SEM data for one contemplated embodiment.

Fig. 28 shows SEM data for contemplated embodiments of the present subject matter.

Fig. 29 graphically illustrates Mw (Daltons) v. Time (Hours) for several contemplated embodiments of the present subject matter.

Fig. 30 graphically illustrates Film Thickness (Angstroms) v. Time (Hours) for several contemplated embodiments of the present subject matter.

Fig. 31 graphically illustrates Delta Thickness (Angstroms) v. Distance Between Vias (nm) for several contemplated embodiments.

Table 1 shows a preliminary aging study using acetone-free and acetone/IPA-free mixtures. POR = control.

Table 2 shows reflux time, temperature, gas chromatography information, thickness, optical properties, ratios of water, ethanol, butanol and PGMEA, density, pH and total percent solids for 6 “runs” of contemplated materials.

Table 3 shows the heat ramp data for the 6 runs represented in Table 2.

Table 4 (parts 1 and 2) shows the summary of the via fill versus the thickness and pitch for several contemplated materials at different pH measurements versus other contemplated materials with high boiling point solvents at different pH measurements.

Table 5 shows the Parent QC results from water control experiments.

Table 6 shows the Child QC results from water control experiments.

Table 7 shows the data collected for Example 4, which is graphically represented in Figure 31.

Table 8 shows etch solution experiments conducted using contemplated compounds of the present subject matter.

DETAILED DESCRIPTION

An anti-reflective coating material for ultraviolet photolithography comprises at least one inorganic-based compound or inorganic material; at least one absorbing compound and at least one material modification agent. The at least one material modification agent may 5 include any compound or composition that can modify the coating material to improve the photolithographic, compatibility and/or physical quality of the resulting film, such as by improving the etch selectivity and/or stripping selectivity or by minimizing the fill bias. The at least one material modification agent may comprise at least one porogen, at least one leveling agent, at least one high-boiling solvent, at least one catalyst, at least one densifying 10 agent, at least one pH tuning agent, at least one capping agent, at least one replacement solvent, at least one adhesion promoter, such as a resin-based material and/or a combination thereof that are incorporated into the inorganic-based material or compound. Resin-based adhesion promoters may comprise organic resins such as phenolic-containing resins, novolac resins, such as CRJ-406 or HRJ-11040 (both from Schenectady International, Inc.), and 15 acrylate resin and/or a styrene resins. Other adhesion promoters may comprise polydimethylsiloxane materials, ethoxy or hydroxy-containing silane monomers, vinyl-containing silane monomers, acrylated silane monomers, or silyl hydrides.

The absorbing compositions are further diluted in appropriate solvents to form coating solutions and applied to various layers of materials in fabricating layered materials, electronic 20 devices, and semiconductor devices. The coating solutions may be applied by any suitable method or process, including spinning onto a surface, dripping onto a surface, rolling onto a surface and/or a combination of any of these methods or processes. The absorbing anti-reflective coatings are designed to be readily integrated into existing layered material, electronic component or semiconductor fabrication processes. Some properties that facilitate 25 integration include a) developer resistance, b) thermal stability during standard photoresist processing, and c) selective removal with respect to underlying layers.

INORGANIC-BASED MATERIALS AND INORGANIC COMPOUNDS

Inorganic-based compounds and/or materials and/or contemplated spin-on inorganic- 30 based compounds and/or materials, such as silicon-based, gallium-based, germanium-based,

arsenic-based, boron-based compounds or combinations thereof are contemplated herein. Examples of silicon-based compounds comprise siloxane compounds, such as methylsiloxane, methylsilsesquioxane, phenylsiloxane, phenylsilsesquioxane, methylphenylsiloxane, methylphenylsilsesquioxane, silazane polymers, dimethylsiloxane, 5 diphenylsiloxane, methylphenylsiloxane, silicate polymers, silsilic acid derivatives, and mixtures thereof. A contemplated silazane polymer is perhydrosilazane, which has a "transparent" polymer backbone where chromophores can be attached.

As used herein, inorganic-based materials, inorganic compounds and spin-on-glass materials also include siloxane polymers and blockpolymers, hydrogensiloxane polymers of 10 the general formula $(H_{0-1.0}SiO_{1.5-2.0})_n$, hydrogensilsesquioxane polymers, which have the formula $(HSiO_{1.5})_n$, where n is greater than about four and derivatives of silsilic acid. Also included are copolymers of hydrogensilsesquioxane and an alkoxyhydridosiloxane or hydroxyhydridosiloxane. Materials contemplated herein additionally include organosiloxane polymers, acrylic siloxane polymers, silsesquioxane-based polymers, derivatives of silici acid, 15 organohydridosiloxane polymers of the general formula $(H_{0-1.0}SiO_{1.5-2.0})_n(R_{0-1.0}SiO_{1.5-2.0})_m$, and organohydridosilsesquioxane polymers of the general formula $(HSiO_{1.5})_n(RSiO_{1.5})_m$, where m is greater than zero and the sum of n and m is greater than about four and R is alkyl or aryl. Some useful organohydridosiloxane polymers have the sum of n and m from about 20 four to about 5000 where R is a C_1-C_{20} alkyl group or a C_6-C_{12} aryl group. The organohydridosiloxane and organohydridosilsesquioxane polymers are alternatively denoted spin-on-polymers. Some specific examples include alkylhydridosiloxanes, such as methylhydridosiloxanes, ethylhydridosiloxanes, propylhydridosiloxanes, t-butylhydridosiloxanes, phenylhydridosiloxanes; and alkylhydridosilsesquioxanes, such as 25 methylhydridosilsesquioxanes, ethylhydridosilsesquioxanes, propylhydridosilsesquioxanes, t-butylhydridosilsesquioxanes, phenylhydridosilsesquioxanes, and combinations thereof.

As used herein, the phrases "spin-on material", "spin-on organic material", "spin-on composition" and "spin-on inorganic composition" may be used interchangeable and refer to those solutions and compositions that can be spun-on to a substrate or surface. It is further contemplated that the phrase "spin-on-glass materials" refers to a subset of "spin-on inorganic materials", in that spin-on glass materials refer to those spin-on materials that comprise silicon-based compounds and/or polymers in whole or in part.

In some contemplated embodiments, specific organohydridosiloxane resins utilized herein have the following general formulas:

	$[H-Si_{1.5}]_n[R-SiO_{1.5}]_m$	Formula (1)
5	$[H_{0.5}-Si_{1.5-1.8}]_n[R_{0.5-1.0}-SiO_{1.5-1.8}]_m$	Formula (2)
	$[H_{0-1.0}-Si_{1.5}]_n[R-SiO_{1.5}]_m$	Formula (3)
	$[H-Si_{1.5}]_x[R-SiO_{1.5}]_y[SiO_2]_z$	Formula (4)

wherein:

10 the sum of n and m, or the sum or x, y and z is from about 8 to about 5000, and m or y is selected such that carbon containing constituents are present in either an amount of less than about 40 percent (Low Organic Content = LOSP) or in an amount greater than about 40 percent (High Organic Content = HOSP); R is selected from substituted and unsubstituted, normal and branched alkyls (methyl, ethyl, butyl, propyl, pentyl), alkenyl groups (vinyl, allyl, 15 isopropenyl), cycloalkyls, cycloalkenyl groups, aryls (phenyl groups, benzyl groups, naphthalenyl groups, anthracenyl groups and phenanthrenyl groups), and mixtures thereof; and wherein the specific mole percent of carbon containing substituents is a function of the ratio of the amounts of starting materials. In some LOSP embodiments, particularly favorable results are obtained with the mole percent of carbon containing substituents being in the range 20 of between about 15 mole percent to about 25 mole percent. In some HOSP embodiments, favorable results are obtained with the mole percent of carbon containing substituents are in the range of between about 55 mole percent to about 75 mole percent.

Several contemplated polymers comprise a polymer backbone encompassing alternate silicon and oxygen atoms. In contrast with previously known organosiloxane resins, some of 25 the polymers and inorganic-based compositions and materials utilized herein have essentially no hydroxyl or alkoxy groups bonded to backbone silicon atoms. Rather, each silicon atom, in addition to the aforementioned backbone oxygen atoms, is bonded only to hydrogen atoms and/or R groups as defined in Formulae 1, 2, 3 and 4. By attaching only hydrogen and/or R groups directly to backbone silicon atoms in the polymer, unwanted chain lengthening and 30 cross-linking is avoided. And given, among other things, that unwanted chain lengthening

and cross-linking is avoided in the resins of the present invention, the shelf life of these resin solutions is enhanced as compared to previously known organosiloxane resins. Furthermore, since silicon-carbon bonds are less reactive than silicon hydrogen bonds, the shelf life of the organohydridosiloxane resin solutions described herein is enhanced as compared to 5 previously known hydridosiloxane resins.

Some of the contemplated compounds previously mentioned are taught by commonly assigned US Patent 6,143,855 and pending US Serial No. 10/078919 filed February 19, 2002; Honeywell International Inc.'s commercially available HOSP® product; nanoporous silica such as taught by commonly assigned US Patent 6,372,666; Honeywell International Inc.'s 10 commercially available NANOGLASS®E product; organosilsesquioxanes taught by commonly assigned WO 01/29052; and fluorosilsesquioxanes taught by commonly assigned US Patent 6,440,550, incorporated herein in their entirety. Other contemplated compounds are described in the following issued patents and pending applications, which are herein incorporated by reference in their entirety: (PCT/US00/15772 filed June 8, 2000; US 15 Application Serial No. 09/330248 filed June 10, 1999; US Application Serial No. 09/491166 filed June 10, 1999; US 6,365,765 issued on April 2, 2002; US 6,268,457 issued on July 31, 2001; US Application Serial No. 10/001143 filed November 10, 2001; US Application Serial No. 09/491166 filed January 26, 2000; PCT/US00/00523 filed January 7, 1999; US 6,177,199 issued January 23, 2001; US 6,358,559 issued March 19, 2002; US 6,218,020 issued April 20 17, 2001; US 6,361,820 issued March 26, 2002; US 6,218,497 issued April 17, 2001; US 6,359,099 issued March 19, 2002; US 6,143,855 issued November 7, 2000; US Application Serial No. 09/611528 filed March 20, 1998; and US Application Serial No. 60/043,261). Silica compounds contemplated herein are those compounds found in US Issued Patents: 6,022,812; 6,037,275; 6,042,994; 6,048,804; 6,090,448; 6,126,733; 6,140,254; 6,204,202; 25 6,208,041; 6,318,124 and 6,319,855.

As used herein, the term "crosslinking" refers to a process in which at least two molecules, or two portions of a long molecule, are joined together by a chemical interaction. Such interactions may occur in many different ways including formation of a covalent bond, formation of hydrogen bonds, hydrophobic, hydrophilic, ionic or electrostatic interaction. 30 Furthermore, molecular interaction may also be characterized by an at least temporary physical connection between a molecule and itself or between two or more molecules.

In some contemplated embodiments, the polymer backbone conformation is a cage configuration. Accordingly, there are only very low levels or reactive terminal moieties in the polymer resin given the cage conformation. A cage conformation of the polymer backbone also ensures that no unwanted chain lengthening polymerization will occur in solution, 5 resulting in an extended shelf life. Each silicon atom of the polymer is bonded to at least three oxygen atoms. Moieties bonded to the polymer backbone include hydrogen and the organic groups described herein. As used herein, the term "backbone" refers to a contiguous chain of atoms or moieties forming a polymeric strand that are covalently bound such that removal of any of the atoms or moiety would result in interruption of the chain.

10 As used herein, the term "monomer" refers to any chemical compound that is capable of forming a covalent bond with itself or a chemically different compound in a repetitive manner. The repetitive bond formation between monomers may lead to a linear, branched, super-branched, or three-dimensional product. Furthermore, monomers may themselves comprise repetitive building blocks, and when polymerized the polymers formed from such 15 monomers are then termed "blockpolymers". Monomers may belong to various chemical classes of molecules including organic, organometallic or inorganic molecules. The molecular weight of monomers may vary greatly between about 40 Dalton and 20000 Dalton. However, especially when monomers comprise repetitive building blocks, monomers may have even higher molecular weights. Monomers may also include additional groups, such as 20 groups used for crosslinking.

In some contemplated embodiments, the molecular weight of the inorganic-based compound may be increased in order to change the solubility of the material. In turn, changing the solubility of the material helps to prevent voiding and increases the planarization ability of the material.

25

ABSORBING COMPOUND

Many naphthalene-, phenanthrene- and anthracene-based compounds have significant absorption at 248 nm and below. Benzene-based, equivalently termed here phenyl-based, compounds have significant absorption at wavelengths shorter than 200 nm. While these 30 naphthalene-, anthracene-, phenanthrene- and phenyl-based compounds are frequently referred to as dyes, the term absorbing compound is used here because the absorptions of

these compounds are not limited to wavelengths in the visible region of the spectrum. However, not all such absorbing compounds can be incorporated into inorganic-based materials for use as anti-reflective coating materials. Preferred absorbing compounds suitable for use have a definable absorption peak centered around wavelengths such as 248 5 nm, 193 nm, 157 nm or other ultraviolet wavelengths, such as 365 nm, that may be used in photolithography. It is contemplated that a preferred "definable absorption peak" is one that is at least 0.5 nm in width, wherein width is calculated by those methods commonly known in the art of photolithography. In more preferred embodiments, the definable absorption peak is at least 1 nm in width. In even more preferred embodiments, the definable absorption peak is 10 at least 5 nm in width. In most preferred embodiments, the definable absorption peak is at least 10 nm in width.

The chromophores of suitable absorbing compounds typically have at least one benzene ring, and where there are two or more benzene rings, the rings may or may not be fused. Incorporatable absorbing compounds have an accessible reactive group attached to the 15 chromophore, wherein the reactive groups include hydroxyl groups, amine groups, carboxylic acid groups, and substituted silyl groups with silicon bonded to one, two, or three "leaving groups," such as alkoxy groups, acetoxy groups or halogen atoms. Ethoxy or methoxy groups or chlorine atoms are frequently used as leaving groups. Preferable reactive groups comprise siliconalkoxy, silicondialkoxy and silicontrialkoxy groups, such as siliconethoxy, 20 silicodiethoxy, silicontriethoxy, siliconmethoxy, silicodimethoxy, and silicontrimethoxy groups and halosilyl groups, such as chlorosilyl, dichlorosilyl, and trichlorosilyl groups, and acetoxy groups like methyltriacetoxy silane, tetraacetoxy silane.

The reactive groups may be directly bonded to the chromophore, as, for example, in phenyltrioxysilane, or the reactive groups may be attached to the chromophore through an 25 ester, a ketone and/or oxygen linkage or a hydrocarbon bridge, as, for example, in 9-anthracene carboxy-alkyl trialkoxysilane. The inclusion of silicontrialkoxy groups on chromophores has been found to be advantageous, especially for promoting stability of the absorbing SOG films. Other useful absorbing compounds are those compounds that contain 30 an azo group, -N=N-, and an accessible reactive group, particularly those containing an azo group linking benzene rings, especially when absorption around 365 nm is desired for the particular application. Azo groups may be included as part of a straight-chain molecule, a cyclic molecule or a hybrid straight-chain/cyclic molecule.

The absorbing compounds may be incorporated interstitially in the inorganic-based material matrix. The absorbing compounds may also be chemically bonded to the inorganic-based material or polymer. In some contemplated embodiments, the incorporatable absorbing compounds form bonds with the inorganic-based material backbone or polymer backbone via the accessible reactive groups.

Absorbing compositions and materials may also comprise a silicon-based compound and an incorporatable absorbing compound that absorbs light at wavelengths less than about 375 nm. Further, it is contemplated that in other embodiments at least one of the silicon-based compound or the incorporatable absorbing compound comprises at least one alkyl group, alkoxy group, ketone group, acetoxy group, or azo group.

Examples of absorbing compounds suitable for use include those absorbing compounds that have a definable absorption peak around wavelengths less than about 375 nm, such as 365 nm, 248 nm, 193 nm and 157 nm, which include compounds such as anthraflavic acid (1), 9-anthracene carboxylic acid (2), 9-anthracene methanol (3), 9-anthracene ethanol (4), 9-anthracene propanol (5), 9-anthracene butanol (6), alizarin (7), quinizarin (8), primuline (9), 2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone (10), 2-hydroxy-4-(3-trimethoxysilylpropoxy)-diphenylketone (11), 2-hydroxy-4-(3-tributoxysilylpropoxy)-diphenylketone (12), 2-hydroxy-4-(3-tripropoxysilylpropoxy)-diphenylketone (13), rosolic acid (14), triethoxysilylpropyl-1,8-naphthalimide (15), trimethoxysilylpropyl-1,8-naphthalimide (16), tripropoxysilylpropyl-1,8-naphthalimide (17), 9-anthracene carboxy-methyl triethoxysilane (18), 9-anthracene carboxy-ethyl triethoxysilane (19), 9-anthracene carboxy-butyl triethoxysilane (20), 9-anthracene carboxy-propyl triethoxysilane (21), 9-anthracene carboxy-methyl trimethoxysilane (22), 9-anthracene carboxy-ethyl tributoxysilane (23), 9-anthracene carboxy-methyl tripropoxysilane (24), 9-anthracene carboxy-propyl trimethoxysilane (25), phenyltriethoxysilane (26), phenyltrimethoxysilane (27), phenyltripropoxysilane (28), 10-phenanthrene carboxy-methyl triethoxysilane (29), 10-phenanthrene carboxy-ethyl triethoxysilane (30), 10-phenanthrene carboxy-methyl trimethoxysilane (31), 10-phenanthrene carboxy-propyl triethoxysilane (32), 4-phenylazophenol, (33), 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane (34), 4-methoxyphenylazobenzene-4-carboxy-ethyl triethoxysilane (35), 4-ethoxyphenylazobenzene-4-carboxy-propyl triethoxysilane (36), 4-butoxyphenylazobenzene-4-carboxy-propyl triethoxysilane (37), 4-

methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane (38), 4-
ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane (39), 4-
methoxyphenylazobenzene-4-carboxy-ethyl triethoxysilane (40), 4-
methoxyphenylazobenzene-4-carboxy-propyl triethoxysilane (41), and combinations, thereof.

5 Chemical formulas of absorbing compounds 1 - 41 are illustrated in Figs. 1a - 1f. Advantageous results have been obtained, for example, with 9-anthracene carboxy-methyl triethoxysilane (18) with combinations of 9-anthracene methanol (3), 2-hydroxy-4-(3-triethoxysilylpropoxy)-diphenylketone (10), and rosolic acid (14), and with phenyltriethoxysilane (26). It should be appreciated, however, that this list of specific 10 compounds is not an exhaustive list, and that contemplated and preferred compounds can be selected from the chemical compound classes that comprise these specific compounds. It should also be appreciated that suitable absorbing compounds may be organic-based or inorganic-based compounds. However, in some contemplated embodiments, the absorbing compound may be organic-based, as long as the ARC doesn't share the same chemical 15 properties with the photoresist, which can limit the useable process sequences. However, the class of photoresist materials can be broad because the addition of a material modification agent, such as a pH tuning agent, makes it possible to match any photolithographic resist material with an anti-reflective coating and make them compatible with one another. Examples of some contemplated photolithographic resist materials comprise acrylate-based 20 resist materials, epoxy-based chemically amplified resists, fluoropolymer resists (which are especially useful when contemplating a 157 nm absorption wavelength), poly(norbornene-maleic anhydride) alternating co-polymers, polystyrene systems and diazonaphthoquinone/novolac resists.

Absorbing compounds 1 - 25 and 29-41 are available commercially, for example, 25 from Aldrich Chemical Company (Milwaukee, WI). 9-anthracene carboxy-alkyl trialkoxysilanes are synthesized using esterification methods, as described below in the Examples Section. Absorbing compound 26-28 is available commercially from Gelest, Inc. (Tullytown, PA). Examples of phenyl-based absorbing compounds in addition to absorbing compound (26-28), many of which are also commercially available from Gelest, Inc., include 30 structures with silicon-based reactive groups attached to phenyl rings or to substituted phenyls, such as methylphenyl, chlorophenyl, and chloromethylphenyl. Specific phenyl-based absorbing compounds include phenyltrimethoxysilane, benzyltrichlorosilane,

chloromethylphenyltrimethoxysilane, phenyltrifluorosilane, to name only a few examples. Diphenyl silanes including one or two "leaving groups," such as diphenylmethylethoxysilane, diphenyldiethoxysilane, and diphenyldichlorosilane, to again name only a few examples, are also suitable incorporatable absorbing compounds. Alkoxybenzoic acids may also be used as 5 absorbing compounds, including methoxybenzoic acid.

A general method of synthesizing 9-anthracene carboxy-alkyl trialkoxysilane compounds comprises using 9-anthracene carboxylic acid and a chloromethyl trialkoxysilane compound as reactants. Specifically, a method of synthesizing 9-anthracene carboxy-methyl triethoxysilane (18) uses 9-anthracene carboxylic acid (2) and chloromethyl triethoxysilane as 10 reactants. The reactants are combined with triethylamine and methylisobutylketone (MIBK), previously dried over 4 Å molecular sieves, to form a reaction mixture which is heated to reflux and refluxed for from approximately 6 to 10 hours. After reflux, the reaction mixture is cooled overnight leading to a large quantity of solid precipitate. The remaining solution is 15 roto-evaporated, filtered through a silica gel column, and roto-evaporated a second time, to produce 9-anthracene carboxy-methyl triethoxysilane (18) as a dark amber oily liquid, which may be purified. This method is significant because it is suitable to use to produce any compound in the class of 9-anthracene carboxy-alkyl trialkoxysilanes, including 9-anthracene carboxy-ethyl triethoxysilane, 9-anthracene carboxy-propyl trimethoxysilane, and 9-anthracene carboxy-propyl triethoxysilane.

20

POROGENS

At least one porogen may be added to the inorganic-based composition or inorganic material in order to increase etch selectivity and/or stripping selectivity of the inorganic-based material or composition. Without being bound to any particular theory, it is understood that 25 in one aspect of the subject matter herein the addition of at least one porogen to the inorganic-based material will result in pores or voids being formed in the material, coating and/or film. The pores or voids may be formed as a result of structural rearrangement or loss of material such that a pore or void or increase in free volume is left behind. The pores or voids in the material, coating and/or film create additional surface area in the coating or film which 30 ultimately increases the etch selectivity and/or stripping selectivity of the material, coating and/or film. In addition, the plasma etch rate of the film will increase with increasing

porosity giving it better dry etch selectivity to photoresist. This dry etch selectivity is necessary to maintain proper transfer of the critical dimension from printing through etch. Adding at least one porogen increases both the dry and wet etch rate of the absorbing material, coating and/or film versus the porogen content without degrading the lithographic 5 performance of the absorbing film's antireflective properties. The porogen's molecular weight can also be used to determine if the porogen is compatible with the inorganic-based compound's matrix in the material. This compatibility quotient is related to the solubility parameters of the inorganic-based compound's matrix. In an ideal case the porogen should match the solubility parameter of the matrix coating formulation before cure, so that when 10 formulation molecular weights are known, appropriate molecular weights of the porogen can be determined by matching the solubility parameters with the matrix. Solubility parameters may be determined experimentally by relationships to the refractive index, dielectric constant, surface tension and intrinsic viscosity, or by calculation using group contribution methods or by molecular models of cohesive energy. (review ref Physical Properties of Polymers 15 Handbook, Chapter 16 "Solubility Parameters" Y. Du, Y. Xue, H.L. Frisch pp 227-239; James E. Mark Ed., 1996, American Institute of Physics, Woodbury, NY)

In another aspect of the subject matter taught herein, the porogen may serve a dual purpose or multi-stage purpose. The porogen may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups. Once the porogen is 20 incorporated into the composition it will act effectively as a "magnet" to attract the stripping and/or etching solution to the porogen by utilizing a difference in polarity between the porogen or by utilizing the functional groups on the porogen. This attraction effect by the porogen can be activated in several ways. For example, there may be an exothermic reaction that takes place when the porogen is incorporated into the absorbing composition at room 25 temperature, there may be an external energy and/or heat that needs to be added to "activate" the porogen or there may be a pressure differential applied to the absorbing composition that will "activate" the porogen. However, whether energy is added or not once the porogen is added, it should be understood that, in this embodiment, the porogen activated to the point where a complete pore or void is formed and the porogen remains until the lithography step is 30 completed. Once the lithography step is completed, the absorbing composition comprising the porogen may be further heated so that the porogen can form a pore or void. At this point, the pores or voids in the material, coating and/or film create additional surface area in the

coating or film which ultimately increases the etch selectivity and/or stripping selectivity of the material, coating and/or film, as described in the earlier embodiments.

As used herein, the term "pore" includes voids and cells in a material and any other term meaning space occupied by gas in the material. The term "pore" may also include a differential in material density wherein the free volume has been increased ("porous nature" has been introduced). Appropriate gases include relatively pure gases and mixtures thereof. Air, which is predominantly a mixture of N₂ and O₂ is commonly distributed in the pores, but pure gases such as nitrogen, helium, argon, CO₂ or CO are also contemplated. Pores are typically spherical but may alternatively or additionally include tubular, lamellar, discoidal, voids having other shapes, or a combination of the preceding shapes and may be open or closed. The term "porogen" as used herein may have a variety of mechanisms available to form the pore but in general is a material which upon removal leaves behind either a "pore" or a "void" or a material that can rearrange to create a "pore" or "void". In one embodiment, a porogen is a decomposable material that is radiation, thermally, chemically or moisture decomposable, degradable, depolymerizable or otherwise capable of breaking down and includes solid, liquid or gaseous material.

The decomposed porogen is removable from or can volatilize or diffuse through a partially or fully cross-linked matrix to create pores in a subsequently fully-cured matrix and thus, lower the matrix's dielectric constant and enhance the sacrificial properties. In another embodiment, the porogen might be a material, which does not decompose but can be dissolved out of the matrix leaving behind the "pore". In a third embodiment the porogen might be a material that does not decompose but is volatile enough to dissipate at specific elevated temperatures such as in the 250-350°C range. Supercritical materials, such as CO₂, may be used to remove the porogen and decomposed porogen fragments. Preferably, for a thermally decomposable porogen, the porogen comprises a material having a decomposition temperature greater than the minimum crosslinking temperature of the material. Preferably, the present novel porogens have a degradation or decomposition temperature of up to about 300°C, and in some cases greater than about 300°C. Preferably, the degraded or decomposed porogens volatilize at a temperature greater than the minimum cross-linking temperature of the material with which the porogen is combined. Preferably, the degraded or decomposed porogens volatilize at a temperature between about 50° to about 450°C.

Although International Patent Publication WO 00/31183 teaches that a porogen may be added to thermosettable benzocyclobutene, polyarylene or thermosettable perfluoroethylene monomer to increase porosity thereof and thus, lower the dielectric constant of that resin, the reference teaches that a porogen that is known to function well with a first matrix system will not necessarily function well with another matrix system.

Known porogens, such as linear polymer, star polymers, cross-linked polymeric nanospheres, block copolymers, and hyperbranched polymers may be used in contemplated embodiments with the inorganic-based compounds and materials. Suitable linear polymers are polyethers, such as poly(ethylene oxide) and poly(propylene oxide); polyacrylates such as poly(methylmethacrylate); aliphatic polycarbonates such as poly(propylene carbonate) and poly(ethylene carbonate); polyesters; polysulfones; polystyrene (including monomer units selected from halogenated styrene and hydroxy-substituted styrene); poly(α -methylstyrene); and other vinyl-based polymers. Useful polyester porogens include polycaprolactone; polyethylene terephthalate; poly(oxyadipoyloxy-1,4-phenylene); poly(oxyterephthaloyloxy-1,4-phenylene); poly(oxyadipoyloxy-1,6-hexamethylene); polyglycolide, polylactide (polylactic acid), polylactide-glycolide, polypyruvic acid, polycarbonate such as poly(hexamethylene carbonate) diol having a molecular weight from about 500 to about 2500; and polyether such as poly(bisphenol A-co-epichlorohydrin) having a molecular weight from about 300 to about 6500. Suitable crosslinked, insoluble nanospheres (prepared as nanoemulsions) are suitably comprised of polystyrene or poly(methylmethacrylate). Suitable block copolymers are poly-glycolids, polylactic acid, poly(styrene-co- α -methylstyrene, poly(styrene-ethylene oxide), poly(etherlactones), poly(estercarbonates) and poly(lactonelactide). Suitable hyperbranched polymers are hyperbranched polyester, e.g. hyperbranched poly(caprolactone), and polyethers such as polyethylene oxide and polypropylene oxide. Another useful porogen is ethylene glycol-poly(caprolactone). Useful polymer blocks include polyvinylpyridines, hydrogenated polyvinyl aromatics, polyacrylonitriles, polysiloxanes, polycaprolactams, polyurethanes, polydienes such as polybutadienes and polyisoprenes, polyvinyl chlorides, polyacetals and amine-capped alkylene oxides. Other useful thermoplastic materials include polyisoprenes, polytetrahydrofurans and polyethyloxazolines.

Other suitable porogens suitable for use in contemplated embodiments include polymers, preferably those which contain one or more reactive groups, such as hydroxyl or

amino. Within these general parameters, a suitable polymer porogen for use in the compositions and methods disclosed herein is, e.g. a polyalkylene oxide, a monoether of a polyalkylene oxide, a diether of a polyalkylene oxide, bisether of a polyalkylene oxide, an aliphatic polyester, an acrylic polymer, an acetal polymer, a poly(caprolactone), a poly(valeractone), a poly(methylmethacrylate), a poly(vinylbutyral) and/or combinations thereof. When the porogen is a polyalkylene oxide monoether, one particular embodiment is a C₁ to about C₆ alkyl chain between oxygen atoms and a C₁ to about C₆ alkyl ether moiety, and wherein the alkyl chain is substituted or unsubstituted, e.g., polyethylene glycol monomethyl ether, polyethylene glycol dimethyl ether, or polypropylene glycol monomethyl ether.

Porogens comprising at least two fused aromatic rings wherein each of the fused aromatic rings has at least one alkyl substituent thereon and a bond exists between at least two of the alkyl substituents on adjacent aromatic rings may be used in contemplated embodiments. Preferred porogens include unfunctionalized polyacenaphthylene homopolymer, functionalized polyacenaphthylene homopolymer, the polyacenaphthylene copolymers described below, poly(2-vinylnaphthalene) and vinyl anthracene, and blends with each other. Other useful porogens include adamantane, diamantane, fullerene and polynorbornene. Each of these porogens, including those listed above, may be blended with one another or other porogen material, such as polycaprolactone, polystyrene and polyester. Useful blends include unfunctionalized polyacenaphthylene homopolymer and polycaprolactone. The more preferred porogens are unfunctionalized polyacenaphthylene homopolymer, functionalized polyacenaphthylene homopolymer, polyacenaphthylene copolymer and polynorbornene.

Useful polyacenaphthylene homopolymers may have weight average molecular weights ranging from preferably about 300 to about 20,000; more preferably about 300 to about 10,000; and most preferably about 1000 to about 7000 and may be polymerized from acenaphthylene using different initiators such as 2,2'-azobisisobutyronitrile (AIBN); di-tert-butyl azodicarboxylate; di-phenylazodicarboxylate; 1,1'-azobis(cyclohezanecarbonitrile); benzoyl peroxide (BPO); t-butyl peroxide; and boron trifluoride diethyl etherate. The polyacenaphthylene homopolymer may have functional end groups such as triple bonds or double bonds to the chain end or cationic polymerization quenched with a double or triple

bond alcohol, such as allyl alcohol, propargyl alcohol, butynol, butenol or hydroxyethylmethacrylate.

European Patent Publication 315453 teaches that silica and certain metal oxides may react with carbon to form volatile sub oxides and gaseous carbon oxide to form pores and 5 teaches that sources of carbon include any suitable organic polymer including polyacenaphthylene. However, the reference does not teach or suggest that polyacenaphthylene is a porogen useful in non-metallic materials or in reducing the dielectric constant of a matrix or increasing the etch selectivity of an absorbing spin-on material.

Useful polyacenaphthylene copolymers may be linear polymers, star polymers or 10 hyperbranched polymers. The comonomer may have a bulky side group that will result in copolymer conformation that is similar to that of polyacenaphthylene homopolymer or a nonbulky side group that will result in copolymer conformation that is dissimilar to that of polyacenaphthylene homopolymer. Comonomers having a bulky side group include vinyl pivalate; tert-butyl acrylate; styrene; α -methylstyrene; tert-butylstyrene; 2-vinylnaphthalene; 15 5-vinyl-2-norbornene; vinyl cyclohexane; vinyl cyclopentant; 9-vinylanthracene; 4-vinylbiphenyl; tetraphenylbutadiene; stilbene; tert-butylstilbene; and indene; and preferably vinyl pivalate. Hydridopolycarbosilane may be used as an additional co-monomer or copolymer component with acenaphthylene and at least one of the preceding comonomers. An example of a useful hydridopolycarbosilane has 10% or 75% allyl groups. Comonomers 20 having a nonbulky side group include vinyl acetate, methyl acrylate, methyl methacrylate, and vinyl ether and preferably vinyl acetate.

When discussing pore generation, the term "degrade" refers to the breaking of covalent bonds. Such breaking of bonds may occur in numerous ways including heterolytic and homolytic breakage. The breaking of bonds need not be complete, i.e., not all breakable bonds must be cleaved. Furthermore, the breaking of bonds may occur in some bonds faster than in others. Ester bonds, for example, are generally less stable than amide bonds, and therefore, are cleaved at a faster rate. Breakage of bonds may also result in the release of fragments differing from one another; depending on the chemical composition of the degraded portion.

30 In a preferred embodiment of the pore generation process, for thermally degradable porogens, thermal energy is applied to the porogen containing material to substantially

degrade or decompose the porogen into its starting components or monomers. As used herein, "substantially degrade" preferably means at least about 40 weight percent of the porogen degrades or decomposes. In more preferred embodiments, at least about 50 weight percent of the porogen degrades or decomposes, and in most preferred embodiments, at least about 80 weight percent of the porogen degrades or decomposes. In another embodiment, the porogen is dissolved out in either a separate process stage or in combination with other stages of process, such as during the photolithography development or during the actual wet stripping of the porogen containing material.

For the preferred embodiment, thermal energy is also applied to volatilize the substantially degraded or decomposed porogen out of the absorbing compound matrix. Preferably, the same thermal energy is used for both the degradation and volatilization steps. As the amount of volatilized degraded porogen increases, the resulting porosity of the anti-reflective material, coating and/or film increases.

Any suitable procedure or condition may be used to remove or at least partially remove the at least one porogen, including heat, dissolution in solvents, preferential etching, exposure to radiation, electromagnetic radiation, such as ultraviolet, x-ray, laser or infrared radiation; mechanical energy, such as sonication or physical pressure; or particle radiation, such as gamma ray, alpha particles, neutron beam or electron beam as taught by commonly assigned patent publication PCT/US96/08678 and US Patents 6,042,994; 6,080,526; 20 6,177,143; and 6,235,353, which are incorporated herein by reference in their entireties.

SOLVENTS

At least one high-boiling solvent and/or at least one replacement solvent may be added to the anti-reflective material, coating and/or film. Without being bound to any particular theory, it is understood that the addition of a high-boiling solvent prevents voiding and improves planarization by making the film a "slow drying" film. As used herein, the phrase "high boiling solvents" means that the solvent volatilizes at a temperature at, near and/or preferably slightly above the drying and/or curing temperature of the material, coating and/or film. Preferred high boiling solvents include glycerol, dibutylether, dibutylglycerol, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), N-methyl-pyrrolidone (NMP), di-

methyl-acetamide (DMAc), high boiling aromatic-based solvents, petroleum ether, the carbitol family, and the glycol ether family. High boiling point solvents can also act as porogens, such as dipropylene glycol or ethyl lactate.

At least one replacement solvent may also be used to replace acetone (or another low boiling solvent) in the original anti-reflective coating material in order to improve the planarization of the coating and/or film and decrease voiding. The replacement solvent doesn't necessarily need to be a high-boiling solvent, but must instead improve the planarization ability of the material, coating and/or film over the conventional solvent being used. The replacement solvent may comprise additional functional groups, such as -OH, that have been shown to lead to better strip properties at similar bake temperatures for the solvent being replaced. Without being bound to any particular theory, it is understood that the additional functional groups may cause the replacement solvent to act almost like a porogen would to attract the stripping chemistry into the composition. This porogen-like action may be based on hydrogen-bonding of the replacement solvent with the matrix or the stripping chemistry. Acetone may also be left out of the material, coating or film altogether depending on the improvement to the planarization ability of the material, coating and/or film. Typical replacement solvents comprise isopropylalcohol, propanol, butanol, ethanol, PGMEA, ethyl lactate and/or 2-heptanone.

To further describe the above-contemplated embodiment, the solvent may serve a dual purpose or multi-stage purpose. The solvent may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups other than those characteristics needed by the solvent to blend with or solvate the absorbing composition. Once the solvent is incorporated into the composition it will act effectively as a "magnet" to attract the stripping and/or etching solution to the solvent by utilizing a difference in polarity between the solvent or by utilizing the functional groups on the solvent. This attraction effect by the solvent can be activated in several ways. For example, there may be an exothermic reaction that takes place when the solvent is incorporated into the absorbing composition at room temperature, there may be an external energy and/or heat that needs to be added to "activate" the solvent or there may be a pressure differential applied to the absorbing composition that will "activate" the solvent. However, whether energy is added or not once the solvent is added, it should be understood that, in this embodiment, the solvent is not heated or activated to the point where it is no longer present until the lithography step is

completed. Once the lithography step is completed, the absorbing composition comprising the solvent may be further heated so that the solvent can evaporate. At this point, the coating or film can be further processed, as described in the earlier embodiments.

Typical solvents are also those solvents that are able to solvate the monomers and 5 polymers contemplated herein to be used as absorbing compounds and inorganic-based compounds and materials. Contemplated solvents include any suitable pure or mixture of organic, organometallic or inorganic molecules that are volatilized at a desired temperature. The solvent may also comprise any suitable pure or mixture of polar and non-polar compounds. In preferred embodiments, the solvent comprises water, ethanol, propanol, 10 acetone, toluene, ethers, cyclohexanone, butyrolactone, methylethylketone, methylisobutylketone, N-methylpyrrolidone, polyethyleneglycolmethylether, mesitylene, ethyl lactate, PGMEA, anisole, and families of poly-ether solvents such as carbitols (which constitute a family of ethyleneglycol ethers capped by hydroxy, alkoxy or carboxy groups) and analogous propyleneglycol ethers .

15

CATALYSTS

In other contemplated embodiments, at least one catalyst may be added to the absorbing material in order to improve etch selectivity and/or stripping selectivity. Catalysts may also be added in conjunction with the porogen to expedite pore formation. As used 20 herein, the term "catalyst" means any substance that affects the rate of the chemical reaction without itself being consumed or undergoing a chemical change. Catalysts may be inorganic, organic, or a complex of organic groups and metal halides. Catalysts may also be liquids, solids, gases or a combination thereof. Contemplated catalysts to add irrespective of the porogen addition may comprise acids, such as HNO₃, HCl, lactic acid, acetic acid, oxalic acid, succinic acid, maleic acid and the like. Contemplated porogen depolymerization catalysts include simple acids as described above, superacid photosensitive molecules such as triarylsulfonium, triaryloxonium, or diaryliodonium salts, free radical generators typically used for vinyl-based, acryl-based (and other multiple-bond monomer-based polymers) polymerization and other free-radical based chemistries (such as benozyl peroxide, 25 azobisisobutyronitrile).

ADHESION PROMOTERS

The phrase "adhesion promoter" as used herein means any component that when used with the thermally degradable polymer, improves the adhesion thereof to substrates compared with thermally degradable polymers. Preferably the at least one adhesion promoter is used with the thermally degradable polymer. The adhesion promoter may be a co-monomer reacted with the thermally degradable polymer precursor or an additive to the thermally degradable polymer precursor. Examples of useful adhesion promoters are disclosed in commonly assigned pending US Application Serial Number 158513 filed May 30, 2002 10 incorporated herein in its entirety.

Adhesion promoters contemplated herein may comprise compounds having at least bifunctionality wherein the bifunctionality may be the same or different and at least one of said first functionality and said second functionality is selected from the group consisting of Si-containing groups; N-containing groups; C bonded to O-containing groups; hydroxyl groups; and C double bonded to C-containing groups. The phrase "compound having at least 15 bifunctionality" as used herein means any compound having at least two functional groups capable of interacting or reacting, or forming bonds as follows. The functional groups may react in numerous ways including addition reactions, nucleophilic and electrophilic substitutions or eliminations, radical reactions, etc. Further alternative reactions may also 20 include the formation of non-covalent bonds, such as Van der Waals, electrostatic bonds, ionic bonds, and hydrogen bonds.

In some embodiments of the at least one adhesion promoter, preferably at least one of the first functionality and the second functionality is selected from Si-containing groups; N-containing groups; C bonded to O-containing groups; hydroxyl groups; and C double bonded 25 to C-containing groups. Preferably, the Si-containing groups are selected from Si-H, Si-O, and Si-N; the N-containing groups are selected from such as C-NH₂ or other secondary and tertiary amines, imines, amides, and imides; the C bonded to O-containing groups are selected from =CO, carbonyl groups such as ketones and aldehydes, esters, -COOH, alkoxyls having 1 to 5 carbon atoms, ethers, glycidyl ethers; and epoxies; the hydroxyl group is phenol; and the 30 C double bonded to C-containing groups are selected from allyl and vinyl groups. For

semiconductor applications, the more preferred functional groups include the Si-containing groups; C bonded to O-containing groups; hydroxyl groups; and vinyl groups.

Contemplated adhesion promoters may also comprise an organic resin-based material that further comprises phenolic-containing resins, novolac resins, such as CRJ-406 or HRJ-5 11040 (both from Schenectady International, Inc.), organic acrylate and/or a styrene resins. Other adhesion promoters may comprise polydimethylsiloxane materials, ethoxy or hydroxy-containing silane monomers, vinyl-containing silane monomers, acrylated silane monomers, or silyl hydrides.

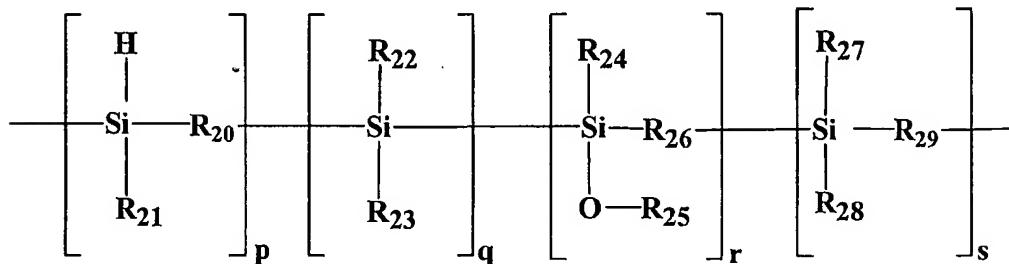
An example of a contemplated adhesion promoter having Si-containing groups is 10 silanes of the Formula I: $(R_{14})_k(R_{15})_lSi(R_{16})_m(R_{17})_n$ wherein R_{14} , R_{15} , R_{16} , and R_{17} each independently represents hydrogen, hydroxyl, unsaturated or saturated alkyl, substituted or unsubstituted alkyl where the substituent is amino or epoxy, saturated or unsaturated alkoxy, unsaturated or saturated carboxylic acid radical, or aryl; at least two of R_{14} , R_{15} , R_{16} , and R_{17} represent hydrogen, hydroxyl, saturated or unsaturated alkoxy, unsaturated alkyl, or 15 unsaturated carboxylic acid radical; and $k+l+m+n \leq 4$. Examples include vinylsilanes such as $H_2C=CHSi(CH_3)_2H$ and $H_2C=CHSi(R_{18})_3$ where R_{18} is CH_3O , C_2H_5O , AcO , $H_2C=CH$, or $H_2C=C(CH_3)O^-$, or vinylphenylmethylsilane; allylsilanes of the formula $H_2C=CHCH_2-Si(OC_2H_5)_3$ and $H_2C=CHCH_2-Si(H)(OCH_3)_2$; glycidoxypropylsilanes such as (3-glycidoxypropyl)methyldiethoxysilane and (3-glycidoxypropyl)trimethoxysilane; 20 methacryloxypropylsilanes of the formula $H_2C=(CH_3)COO(CH_2)_3-Si(OR_{19})_3$ where R_{19} is an alkyl, preferably methyl or ethyl; aminopropylsilane derivatives including $H_2N(CH_2)_3Si(OCH_2CH_3)_3$, $H_2N(CH_2)_3Si(OH)_3$, or $H_2N(CH_2)_3OC(CH_3)_2CH=CHSi(OCH_3)_3$. The aforementioned silanes are commercially available from Gelest.

An example of a preferred adhesion promoter having C bonded to O-containing 25 groups is glycidyl ethers including but not limited to 1,1,1-tris-(hydroxyphenyl)ethane tri-glycidyl ether which is commercially available from TriQuest.

An example of a preferred adhesion promoter having C bonded to O-containing groups is esters of unsaturated carboxylic acids containing at least one carboxylic acid group. Examples include trifunctional methacrylate ester, trifunctional acrylate ester, 30 trimethylolpropane triacrylate, dipentaerythritol pentaacrylate, and glycidyl methacrylate. The foregoing are all commercially available from Sartomer.

An example of a preferred adhesion promoter having vinyl groups is vinyl cyclic pyridine oligomers or polymers wherein the cyclic group is pyridine, aromatic, or heteroaromatic. Useful examples include but not limited to 2-vinylpyridine and 4-vinylpyridine, commercially available from Reilly; vinyl aromatics; and vinyl heteroaromatics including but not limited to vinyl quinoline, vinyl carbazole, vinyl imidazole, and vinyl oxazole.

An example of a preferred adhesion promoter having Si-containing groups is the polycarbosilane disclosed in commonly assigned copending allowed US Patent Application Serial Number 09/471299 filed December 23, 1999 incorporated herein by reference in its entirety. The polycarbosilane is that shown in Formula II:



in which R₂₀, R₂₆, and R₂₉ each independently represents substituted or unsubstituted alkylene, cycloalkylene, vinylene, allylene, or arylene; R₂₁, R₂₂, R₂₃, R₂₄, R₂₇, and R₂₈ each independently represents hydrogen atom or organo group comprising alkyl, alkylene, vinyl, cycloalkyl, allyl, or aryl and may be linear or branched; R₂₅ represents organosilicon, silanyl, siloxyl, or organo group; and p, q, r, and s satisfy the conditions of [4≤ p + q + r + s ≤100,000], and q and r and s may collectively or independently be zero. The organo groups may contain up to 18 carbon atoms but generally contain from about 1 to about 10 carbon atoms. Useful alkyl groups include -CH₂- and -(CH₂)_t where t>1.

Contemplated polycarbosilanes include dihydridopolycarbosilanes in which R₂₀ is a substituted or unsubstituted alkylene or phenyl, R₂₁ group is a hydrogen atom and there are no appendent radicals in the polycarbosilane chain; that is, q, r, and s are all zero. Another preferred group of polycarbosilanes are those in which the R₂₁, R₂₂, R₂₃, R₂₄, R₂₅, and R₂₈ groups of Formula II are substituted or unsubstituted alkenyl groups having from 2 to 10

carbon atoms. The alkenyl group may be ethenyl, propenyl, allyl, butenyl or any other unsaturated organic backbone radical having up to 10 carbon atoms. The alkenyl group may be dienyl in nature and includes unsaturated alkenyl radicals appended or substituted on an otherwise alkyl or unsaturated organic polymer backbone. Examples of these preferred 5 polycarbosilanes include dihydrido or alkenyl substituted polycarbosilanes such as polydihydridocarbosilane, polyallylhydrididocarbosilane and random copolymers of polydihydridocarbosilane and polyallylhydridocarbosilane.

In the more preferred polycarbosilanes, the R_{21} group of Formula II is a hydrogen atom and R_{21} is methylene and the appendent radicals q , r , and s are zero. Other preferred 10 polycarbosilane compounds of the invention are polycarbosilanes of Formula II in which R_{21} and R_{27} are hydrogen, R_{20} and R_{29} are methylene, and R_{28} is an alkenyl, and appendent radicals q and r are zero. The polycarbosilanes may be prepared from well known prior art processes or provided by manufacturers of polycarbosilane compositions. In the most preferred polycarbosilanes, the R_{21} group of Formula II is a hydrogen atom; R_{24} is $-CH_2-$; q , r , 15 and s are zero and p is from 5 to 25. These most preferred polycarbosilanes may be obtained from Starfire Systems, Inc. Specific examples of these most preferred polycarbosilanes follow:

Polycarbosilane	Weight Average Molecular Weight (Mw)	Polydispersity	Peak Molecular Weight (Mp)
1	400-1,400	2-2.5	330-500
2	330	1.14	320
3 (with 10% allyl groups)	10,000-14,000	10.4-16	1160
4 (with 75% allyl groups)	2,400	3.7	410

20 As can be observed in Formula II, the polycarbosilanes utilized may contain oxidized radicals in the form of siloxyl groups when $r > 0$. Accordingly, R_{25} represents organosilicon, silanyl, siloxyl, or organo group when $r > 0$. It is to be appreciated that the oxidized versions of the polycarbosilanes ($r > 0$) operate very effectively in, and are well within the purview of the present invention. As is equally apparent, r can be zero independently of p , q , and s the 25 only conditions being that the radicals p , q , r , and s of the Formula II polycarbosilanes must satisfy the conditions of $[4 < p + q + r + s < 100,000]$, and q and r can collectively or independently be zero.

The polycarbosilane may be produced from starting materials that are presently commercially available from many manufacturers and by using conventional polymerization processes. As an example of synthesis of the polycarbosilanes, the starting materials may be produced from common organo silane compounds or from polysilane as a starting material by 5 heating an admixture of polysilane with polyborosiloxane in an inert atmosphere to thereby produce the corresponding polymer or by heating an admixture of polysilane with a low molecular weight carbosilane in an inert atmosphere to thereby produce the corresponding polymer or by heating an admixture of polysilane with a low molecular carbosilane in an inert atmosphere and in the presence of a catalyst such as polyborodiphenylsiloxane to 10 thereby produce the corresponding polymer. Polycarbosilanes may also be synthesized by Grignard Reaction reported in U.S. Patent 5,153,295 hereby incorporated by reference in its entirety.

An example of a preferred adhesion promoter having hydroxyl groups is phenol-formaldehyde resins or oligomers of the Formula III: $-[R_{30}C_6H_2(OH)(R_{31})]_u-$ where R₃₀ is substituted or unsubstituted alkylene, cycloalkylene, vinyl, allyl, or aryl; R₃₁ is alkyl, alkylene, vinylene, cycloalkylene, allylene, or aryl; and u=3-100. Examples of useful alkyl groups include $-CH_2-$ and $-(CH_2)_v-$ where v>1. A particularly useful phenol-formaldehyde resin oligomer has a molecular weight of 1500 and is commercially available from Schenectady International Inc.

20 The present adhesion promoter is added in small, effective amounts preferably from about 0.01% up to about 15% and more preferably from about 0.05% to about 7% based on the weight of the present thermally degradable polymer.

The adhesion promoter may also serve a dual purpose or multi-stage purpose. The adhesion promoter may be specifically chosen for a particular absorbing composition based 25 on polarity and/or functional groups other than those characteristics needed by the adhesion promoter in order to promote adhesion in the absorbing composition. Once the adhesion promoter is incorporated into the composition it will act effectively as a "magnet" to attract the stripping and/or etching solution to the adhesion promoter by utilizing a difference in polarity between the adhesion promoter or by utilizing the functional groups on the adhesion promoter. This attraction effect by the adhesion promoter can be activated in several ways. 30 For example, there may be an exothermic reaction that takes place when the adhesion promoter is incorporated into the absorbing composition at room temperature, there may be

an external energy and/or heat that needs to be added to "activate" the adhesion promoter, there may not need to be any energy added to the composition depending on the chemical composition of the adhesion promoter, or there may be a pressure differential applied to the absorbing composition that will "activate" the adhesion promoter. However, whether energy 5 is added or not once the adhesion promoter is added, it should be understood that, in this embodiment, the adhesion promoter is not heated or activated to the point where it is chemically modified or broken down until the lithography step is completed. Once the lithography step is completed, the absorbing composition comprising the adhesion promoter may be left unheated or further heated so that the adhesion promoter's chemical composition 10 can change to make it further compatible with the composition. At this point, the coating or film can be further processed, as described in the earlier embodiments.

pH TUNING AGENT

15 The pH tuning agent is a compound, material or solution that is added to the mixture of the inorganic-based material and the absorbing compound in order to "tune" or adjust the pH of the final absorbing composition so that it is compatible or more compatible with any chosen resist material, including those with absorption peaks around 365 nm, 248 nm, 193 nm and 157 nm. pH tuning agents contemplated herein are those also found in commonly assigned PCT Application Serial No.: PCT/US01/45306 filed on November 15, 2001.

20 It should be appreciated, however, that the pH tuning agent not only adjusts the pH of the absorbing material, coating and/or film, but it also influences the chemical performance and characteristics, mechanical performance and structural makeup of the absorbing material, coating and/or film that is part of the layered material, electronic component or semiconductor component, such that the absorbing material, coating and/or film is more 25 compatible with the resist material that is coupled to it. More specifically, the pH tuning agent strongly influences the polymeric characteristics, the structural makeup and the spatial orientation that results in optimized film architecture by increasing the surface properties of the anti-reflective coating for optimal resist performance. In other words, a pH tuning agent that merely adjusts the pH of the spin-on material without influencing the mechanical 30 properties and structural makeup of the absorbing material, coating and/or film or the coupled resist material is not contemplated herein. Also, it should be understood that several pH

tuning agents may also be appropriate as densifying agents, catalysts or both. Each of the material modification agents discussed herein may be classified in more than one category.

Contemplated pH tuning agents must perform two separate and sometimes related functions: a) to influence the pH of the composition to which it is being added; and b) to influence the mechanical performance and/or structural makeup of the absorbing material, coating and/or film, which can also been stated as strongly influencing the polymeric characteristics, the structural makeup and the spatial orientation that results in enhancing the surface properties of the anti-reflective coating for optimal resist performance.

Contemplated pH tuning agents are partly designed to influence the pH of the composition to which it is added. The class of potential pH tuning agents comprises a) any suitable acidic or basic solution, compound, and/or component and/or b) any suitable strength or concentration of an acidic or basic solution, compound and/or component. This compilation of suitable pH "influencers" is the larger set of compound from which the ultimate pH tuning agent is chosen, because the pH "influencer" must also be able to influence the mechanical performance and/or structural makeup of the absorbing material, coating and/or film while also making the absorbing material, coating and/or film compatible or more compatible. By this, for example, it is meant that the chosen pH tuning agent is also designed to match the solubility parameter, the molecular weight, the melting point or some other physical characteristic of the spin-on material and organic absorbing compound mixture. In other words, the pH tuning agent and the mixture of inorganic matrix material and absorbing compound cannot be physically incompatible, depending on the desirable physical characteristic, even if the pH tuning agent performs its first function of influencing the pH of the mixture. In preferred embodiments, the desirable physical characteristic is the solubility parameter or the molecular weight. In more preferred embodiments, the desirable physical characteristic is the solubility parameter.

It is also contemplated that the pH tuning agent will also mechanically and structurally influence the performance and characteristics of the resist material/ARC couple. For example, a pH tuned absorbing material, coating and/or film is applied to a substrate or layered material, and then a resist material is applied to the absorbing material, coating and/or film. When the resist material is exposed and subsequently developed will have an 85-90 degree angle with respect to the absorbing material, coating and/or film (a development line).

In other words, the resist material will not “fall over” onto the absorbing material, coating and/or film, but instead will have a useful development line. In the case where the absorbing material, coating and/or film is not pH tuned, the resist material may “fall over” onto the absorbing material, coating and/or film after etching, which obviously leads a defective resist material and/or to a defective layered material. It is in this instance where the pH tuned absorbing material, coating and/or film influences the mechanical and structural integrity of the absorbing material, coating and/or film and the compatibility of the resist material/ARC couple. As used herein, the terms “coupled” or “couple” mean that the two materials or compositions are juxtaposed on top of one another to the point where the two materials are physically, mechanically and/or chemically bonded to one another.

Examples of some suitable pH tuning agents comprise various molar concentrations of the class of amines, such as γ -aminoalkyltrialkoxysilanes, specifically γ -aminopropyltriethoxysilanes (APTF or APTEOS); water; oxides and alkoxides, such as sodium alkoxides, potassium alkoxides, potassium hydroxide; hydrogen halides, such as hydrogen bromide, hydrochloric acid; acetic acid; sulfuric acid, lactic acid, nitric acid; TMAH; propylene glycol methyl ether acetate (PGMEA); amine-based oligomers, including those oligomers with inorganic atoms such as silicon, and combinations thereof. Contemplated molar concentrations of the pH tuning agent include pure, 10 Molar, 1.0 Molar, 0.1 Molar and 0.01 Molar concentrations, depending on the pH agent chosen for the resist material.

In yet other embodiments, increased pH solutions result in films that exhibit characteristics of being denser than films cast from non-pH tuned solutions. Wet strip tests were used to determine extent of densification. The effect ARC density as on the photoresist process is follows. If the ARC is not dense enough too much photogenerated acid within the resist (generated during exposure of the photoresist to UV radiation) diffuses across the photoresist – ARC boundary resulting in a decrease in the local concentration of photoacid resulting in a degradation of the local acid catalyzed reactions resulting in an under reacted resist which can lead to resist footing (positive tone resist). Opposite to this, if the ARC layer is too dense then an accumulation of local photo generated acid occurs at the interface resulting in an increase in the local acid catalyzed reactions resulting in an over reacted resist which can lead to resist undercut (positive tone resist).

In another embodiment the pH tuning agent may be found on a solid-support material (such as a propylamine-attached silica, amine-based polymers such as melamine, or other amine-attached materials that are insoluble in the process solvent conditions) that is physically separated from the formulation. For instance the pH may be tuned while the 5 formulation is passed thru the solid support material or the pH may be tuned in a slurry with the solid support material, which is later filtered.

The pH tuning agent may also serve a dual purpose or multi-stage purpose. The pH tuning agent may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups other than those characteristics needed by the pH tuning 10 agent in order to "tune" the absorbing composition. Once the pH tuning agent is incorporated into the composition it will act effectively as a "magnet" to attract the stripping and/or etching solution to the pH tuning agent by utilizing a difference in polarity between the pH tuning agent or by utilizing the functional groups on the pH tuning agent. This attraction effect by the pH tuning agent can be activated in several ways. For example, there may be an 15 exothermic reaction that takes place when the pH tuning agent is incorporated into the absorbing composition at room temperature, there may be an external energy and/or heat that needs to be added to "activate" the pH tuning agent, there may not need to be any energy added to the composition depending on the chemical composition of the pH tuning agent, or there may be a pressure differential applied to the absorbing composition that will "activate" 20 the pH tuning agent. However, whether energy is added or not once the pH tuning agent is added, it should be understood that, in this embodiment, the pH tuning agent is not heated or activated to the point where it is chemically modified or broken down until the lithography step is completed. Once the lithography step is completed, the absorbing composition comprising the pH tuning agent may be left unheated or further heated so that the pH tuning 25 agent's chemical composition can change to make it further compatible with the composition. At this point, the coating or film can be further processed, as described in the earlier embodiments.

DENSIFYING AGENT

30 At least one densifying agent may be added to the absorbing compositions disclosed herein. The densifying agent or compound is similar to those previously mentioned in other

material modification sections. It should be understood that many of the compounds mentioned in this and other sections overlap in that some of these compounds may be densifying agents and catalysts or densifying agents and pH tuning agents. The densifying agent comprises at least one compound, material or solution that is added to the absorbing compositions described herein in order to "tune" or adjust the density of the final composition so that the density or other related physical characteristics of the final material are increased relative to the reference material. As used herein, the "reference material" is that material that comprises each component of the contemplated composition described herein except the densifying agent. The "reference material" is meant to be a benchmark composition to which contemplated compositions may be compared.

It should be appreciated, however, that the densifying agent not only adjusts the density of the absorbing composition, but it also influences the chemical performance and characteristics, mechanical performance and structural makeup of the final composition that is part of the layered material, electronic component or semiconductor component, such that the final composition is more compatible with the resist material that is coupled to it. More specifically, the densifying agent strongly influences the polymeric characteristics, the structural makeup and the spatial orientation that results in increasing the surface properties of the underlying coating, including not only anti-reflective coatings but other layers and layered materials, for optimal resist performance.

Like other material modification agents disclosed herein, contemplated densifying agents must perform two separate and sometimes related functions: a) to influence the physical properties of the composition to which it is being added; and b) to influence the mechanical performance and/or structural makeup of the composition, which can also be stated as strongly influencing the polymeric characteristics, the structural makeup and the spatial orientation that results in increasing the surface properties of the layer, coating and/or material, such as an anti-reflective coating, for optimal resist and/or component performance.

Contemplated densifying agents are partly designed to influence the density of the composition to which it is added. The class of potential densifying agents comprises a) any suitable acidic or basic solution, compound, and/or component and/or b) any suitable strength or concentration of an acidic or basic solution, compound and/or component. This compilation of suitable density "influencers" is the larger set of compound from which the

ultimate densifying agent is chosen, because the density "influencer" must also be able to influence the mechanical performance and/or structural makeup of the final composition while also making the final absorbing composition compatible or more compatible. By this, for example, it is meant that the chosen densifying agent is also designed to match the 5 solubility parameter, the molecular weight, the melting point or some other physical characteristic of the inorganic materials, spin-on inorganic materials and/or spin-on-glass materials. In other words, the densifying agent and the inorganic materials, spin-on inorganic materials and/or spin-on-glass materials cannot be physically incompatible, depending on the desirable physical characteristic. In preferred embodiments, the desirable physical 10 characteristic is the solubility parameter or the molecular weight. In more preferred embodiments, the desirable physical characteristic is the solubility parameter.

Examples of some suitable densifying agents or density-tuning agents comprise various molar concentrations of the class of amines, such as γ -aminoalkyltrialkoxysilanes and nitrogen-based salts of those silane compounds, specifically γ -aminopropyltriethoxysilanes 15 (APTEOS) and APTEOS-N; water; oxides and alkoxides, such as sodium alkoxides, potassium alkoxides, potassium hydroxide; hydrogen halides, such as hydrogen bromide, hydrochloric acid; acetic acid; sulfuric acid, lactic acid, nitric acid; TMAH; acetate-based compounds, such as tetra-methyl ammonium acetate (TMAA), APTEOS-acetate and ammonium acetate; nitrate-based compounds, such as tetra-methyl ammonium nitrate 20 (TMAN - a nitric acid stabilized form of TMAA) and ammonium nitrate; amine-based oligomers, including those oligomers with inorganic atoms such as silicon, and combinations thereof. Contemplated molar concentrations of the densifying agent include pure, 10 Molar, 1.0 Molar, 0.1 Molar and 0.01 Molar concentrations, depending on the densifying agent chosen for the resist material.

25 One contemplated method of making a contemplated composition includes combining at least one absorbing composition, at least one densifying agent (material modification agent), an acid/water mixture, such as a nitric acid/water mixture, and at least one solvent to form a reaction mixture; and refluxing the reaction mixture to form the contemplated composition. The composition formed is then diluted with at least one solvent to provide 30 coating solutions that produce films of various thicknesses. The densifying agent may also and alternatively be added during the refluxing step or after the refluxing step. The densifying agent may also be added during the dilution stage where the thickness of the films

is being determined. In other suitable embodiments as mentioned, an incorporatable absorbing compound may be added during the steps used to form the reaction mixture.

In another contemplated method of making a contemplated composition, at least one absorbing composition, at least one densifying agent, and at least one solvent can be 5 combined to form a reaction mixture. The reaction mixture is then refluxed to form the contemplated composition. The composition formed is diluted with at least one solvent to provide coating solutions that produce films of various thicknesses. The densifying agent in this method may either be a variation of the conventional acid/water mixture, in that a different acid may be added, less acid may be added, or more water may be added. The 10 densifying agent may also be added during the dilution step.

More specifically, a reaction mixture including silane reactants, for example HTEOS, or TEOS and MTEOS, or, TMOS and MTMOS; or, alternatively, tetrachlorosilane and methyltrichlorosilane, at least one densifying agent, such as APTEOS-N or APTEOS; a solvent or combination of solvents; and an acid/water mixture, is formed in a reaction vessel. 15 Appropriate solvents include acetone, 2-propanol, and other simple alcohols, ketones and esters such as 1-propanol, MIBK, propoxypropanol, and propyl acetate. The acid/water mixture is, for example nitric acid and water. Other protic acids or acid anhydrides, such as acetic acid, formic acid, phosphoric acid, hydrochloric acid or acetic anhydride are alternatively used in the acid mixture. The resulting mixture is refluxed for between 20 approximately 1 and 24 hours to produce the absorbing composition. As mentioned earlier, the densifying agent may be added during or after the refluxing step, depending on the resist material chosen. Also, as mentioned earlier, the acid concentration and/or strength and the water concentration in the acid/water mixture may be varied in order to become a densifying agent, depending on the resist material chosen for the specific layered material, electronic 25 component or semiconductor component application.

The density-tuned coating solutions (which may or may not be absorbing coating solutions) are applied to various substrates to form layered materials, layers used in semiconductor processing, or layers used in electronic components, depending on the specific fabrication process, typically by conventional spin-on deposition techniques. These 30 techniques include a dispense spin, a thickness spin, and thermal bake steps, to produce suitable coating. Typical processes include a thickness spin of between 1000 and 4000 rpm

for about 20 seconds and two or three bake steps at temperatures between 80°C and 300°C for about one minute each. The density-tuned coatings, according to the present invention exhibit refractive indices between about 1.3 and about 2.0 and extinction coefficients greater than approximately 0.07. It should also be noted that the density-tuned coatings contemplated herein have increased refractive index measurements relative to their non-density-tuned counterparts.

CAPPING AGENT

At least one capping agent may also be added to the absorbing composition as a material modification agent. As used herein, the term "capping agent" means a terminating monomer that effectively controls the molecular weight of a particular polymer by "capping" the end of the polymer. In contemplated embodiments, the capping agent comprises a silane monomer with only one reactive group, such as an ethoxy reactive group, with the rest of the monomer being methyl groups. Furthermore, the silane monomer is added late in the parent reaction that forms the absorbing composition. Any suitable terminating monomer may be used in this application, including silane compositions such as TMEOS.

The capping agent may also serve a dual purpose or multi-stage purpose. The capping agent may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups other than those characteristics needed by the capping agent in order to cap all or part of the constituents of the absorbing composition. By controlling molecular weight and the polarity of the functional groups present, the capping agent may also function to adjust solubility parameter of the matrix material which improves it's solubility compatibility throughout the process. Once the capping agent is incorporated into the composition it will act effectively as a "magnet" to attract the stripping and/or etching solution to the capping agent or the compound comprising the capping agent by utilizing a difference in polarity between the capping agent or by utilizing the functional groups on the capping agent. This attraction effect by the capping agent can be activated in several ways. For example, there may be an exothermic reaction that takes place when the capping agent is incorporated into the absorbing composition at room temperature, there may be an external energy and/or heat that needs to be added to "activate" the capping agent, there may not need to be any energy added to the composition depending on the chemical composition of the

capping agent, or there may be a pressure differential applied to the absorbing composition that will “activate” the capping agent. However, whether energy is added or not once the capping agent is added, it should be understood that, in this embodiment, the capping agent is not heated or activated to the point where it is chemically modified or broken down until the 5 lithography step is completed. Once the lithography step is completed, the absorbing composition comprising the capping agent may be left unheated or further heated so that the capping agent’s chemical composition can change to make it further compatible with the composition. At this point, the coating or film can be further processed, as described in the earlier embodiments.

10

LEVELING AGENT

At least one leveling agent may also be added to the absorbing composition as a material modification agent. As contemplated herein, the at least one leveling agent is added to the absorbing composition to improve the via fill bias in the material. Contemplated 15 leveling agents comprise polyacrylates – both ionic and non-ionic, such as BYK 380 and BYK 381.

The leveling agent may also serve a dual purpose or multi-stage purpose. The leveling agent may be specifically chosen for a particular absorbing composition based on polarity and/or functional groups other than those characteristics needed by the leveling agent in order 20 to help level or planarize all or part of the absorbing composition. Once the leveling agent is incorporated into the composition it will act effectively as a “magnet” to attract the stripping and/or etching solution to the leveling agent or the compound comprising the leveling agent by utilizing a difference in polarity between the leveling agent or by utilizing the functional groups on the leveling agent. This attraction effect by the leveling agent can be activated in 25 several ways. For example, there may be an exothermic reaction that takes place when the leveling agent is incorporated into the absorbing composition at room temperature, there may be an external energy and/or heat that needs to be added to “activate” the leveling agent, there may not need to be any energy added to the composition depending on the chemical composition of the leveling agent, or there may be a pressure differential applied to the 30 absorbing composition that will “activate” the leveling agent. However, whether energy is added or not once the leveling agent is added, it should be understood that, in this

embodiment, the leveling agent is not heated or activated to the point where it is chemically modified or broken down until the lithography step is completed. Once the lithography step is completed, the absorbing composition comprising the leveling agent may be left unheated or further heated so that the leveling agent's chemical composition can change to make it further compatible with the composition. At this point, the coating or film can be further processed, as described in the earlier embodiments.

METHODS OF PRODUCTION

According to another aspect of the subject, methods for synthesizing the absorbing compositions described herein are provided. Absorbing materials are typically synthesized from a variety of silane reactants including, for example, triethoxysilane (HTEOS), tetraethoxysilane (TEOS), methyltriethoxysilane (MTEOS), dimethyldiethoxysilane, tetramethoxysilane (TMOS), dimethyldiethoxysilane, methyltrimethoxysilane (MTMOS), trimethoxysilane, dimethyldimethoxysilane, trimethylethoxysilane (TMEOS), phenyltriethoxysilane (PTEOS), phenyltrimethoxysilane (PTMOS), diphenyldiethoxysilane, diphenyldimethoxysilane, tetracetoxysilane (TAS), methyltriacetoxysilane (MTAS), phenyltriacetoxysilane (PTAS), dimethyldiacetoxysilane, and, diphenyldiacetoxysilane. However, gallium, arsenic, germanium, boron and similar atoms and materials may also be used in conjunction with silicon atoms or as the sole atomic material to produce an absorbing material.

Halosilanes, including chlorosilanes, such as trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane, tetrachlorosilane, dichlorosilane, methyldichlorosilane, dimethyldichlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane, chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane, 25 chloromethyltrimethoxysilane, chloroethyltrimethoxysilane, and chlorophenyltrimethoxysilane are also used as silane reactants.

In general, to produce the absorbing compositions, the absorbing compounds, such as absorbing compounds 1 - 41, or combinations thereof, are combined with the silane reactants during the synthesis of the absorbing materials. The material modification agent, such as the 30 at least one porogen, the at least one high-boiling solvent, the at least one leveling agent, the

at least one densifying agent, the at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof may also be combined with the silane reactants during the synthesis of the absorbing materials or once the synthesis is complete, as in the 5 case of the at least one capping agent.

One contemplated method of making an absorbing composition includes combining at least one inorganic-based composition, at least one incorporatable absorbing compound, at least one material modification agent, such as the at least one porogen, the at least one high-boiling solvent, the at least one leveling agent, the at least one densifying agent, the at least 10 one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof, an acid/water mixture, such as a nitric acid/water mixture, and at least one solvent to form a reaction mixture; and heating to a temperature about or above 40°C or refluxing the reaction mixture to form the absorbing composition. The absorbing composition formed is then 15 diluted with at least one solvent to provide coating solutions that produce films of various thicknesses. The material modification agent, such as the at least one porogen, the at least one high-boiling solvent, the at least one leveling agent, the at least one densifying agent, the at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination 20 thereof may also and alternatively be added during the refluxing step or after the refluxing / heating step.

In another contemplated method of making an absorbing composition, at least one inorganic-based composition, at least one incorporatable absorbing compound, at least one material modification agent, such as the at least one porogen, the at least one high-boiling 25 solvent, the at least one leveling agent, the at least one densifying agent, the at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof, and at least one additional solvent can be combined to form a reaction mixture. The reaction mixture is then heating to a temperature about or above 40°C or refluxed to form the 30 absorbing composition. The absorbing composition formed is diluted with at least one solvent to provide coating solutions that produce films of various thicknesses. The pH tuning agent in this method may either be a variation of the conventional acid/water mixture,

in that a different acid may be added, less acid may be added, or more water may be added. Regardless of the pH tuning agent chosen, however, the basic principal still remains – which is that not only the pH is influenced by the pH tuning agent, but the chemical, mechanical and physical properties of the ARC are also influenced resulting in a more compatible resist/ARC couple.

More specifically, a reaction mixture including silane reactants, for example HTEOS, or TEOS and MTEOS, TMEOS or TMOS and MTMOS; or, alternatively, tetrachlorosilane and methyltrichlorosilane, at least one absorbing compound, such as absorbing compounds 1 - 41; at least one pH tuning agent, such as APTF; a solvent or combination of solvents; and an acid/water mixture, is formed in a reaction vessel. Appropriate solvents include acetone, 2-propanol, and other simple alcohols, ketones and esters such as 1-propanol, MIBK, propoxypropanol, and propyl acetate. The acid/water mixture is, for example nitric acid and water. Other protic acids or acid anhydrides, such as acetic acid, lactic acid, oxalic acid, formic acid, phosphoric acid, hydrochloric acid or acetic anhydride are alternatively used in the acid mixture. The resulting mixture is heated to a temperature about or above 40°C or refluxed for between approximately 1 and 24 hours to produce the absorbing solution. As mentioned earlier, the material modification agent, such as the at least one porogen, the at least one high-boiling solvent, the at least one leveling agent, the at least one densifying agent, the at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof may be added during or after the heating / refluxing step, depending on the resist material chosen. Also, as mentioned earlier, the acid concentration and/or strength and the water concentration in the acid/water mixture may be varied in order to become a pH tuning agent, depending on the resist material chosen for the specific layered material, electronic component or semiconductor component application.

The absorbing material can be diluted with appropriate solvents to achieve coating solutions that produce films of various thicknesses. Suitable dilutant solvents include acetone, 2-propanol, ethanol, butanol, methanol, propylacetate, ethyl lactate, propylene glycol methyl ether acetate, and propylene glycol propyl ether, referred to commercially as Propasol-P. Dilutant solvents with high boiling points such as ethyl lactate and propylene glycol propyl ether have been found beneficial. It is believed high boiling point solvents decrease the probability of formation of bubble film defects. In contrast, lower boiling point solvents may

become entrapped below a crosslinked top layer of a film and subsequently produce voids when driven off during a baking process step. Additional solvents useful in the invention include ethylene glycol dimethyl ether, alternatively termed glyme, anisole, dibutyl ether, dipropyl ether, propylene glycol methyl ether acetate, and pentanol. Optionally, surfactants, 5 can be utilized and data/observations for these optional surfactants are presented below in the Examples section; however, these data and observations are not exhaustive of the studies conducted and do not represent all of the surfactants tested. For example, the following classes of surfactants were tested: polyacrylates (both ionic and non-ionic) (BYK brand surfactants, specifically BYK 306, 307, 308, 380 and 381), functional polydimethylsiloxanes 10 (Tagopren brand surfactants), silicones, fluorinated alkylesters (FC brand surfactants, specifically FC4430, FC430 or FC4432 provided by 3M (Minneapolis, MN)), polyether and aliphatic hydrocarbon chain surfactants (Brij surfactants), the product Megafac R08 (provided by DIC (Japan)), or generally the class of fluorocarbon surfactants, are also added to the coating solution. Furthermore, several viscosity agents may be added to the coating 15 solution to effect the viscosity of the coating solution, such as BYK 410 and BYK 420. The coating solution is typically between about 0.5 and 20 % polymer by weight. Prior to use, the coating solution is filtered by standard filtration techniques.

According to a second method of forming absorbing materials, a reaction mixture including at least one silane reactant, at least one absorbing compound, such as absorbing 20 compounds 1 - 41, at least one material modification agent, including the at least one porogen, the at least one high-boiling solvent, the at least one leveling agent, the at least one densifying agent, the at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof, and an additional solvent or combination of solvents is formed 25 in a reaction vessel. The reaction mixture is heated to about or above a temperature of 40°C and held at the desired temperature for between approximately 1 and 24 hours. The silane reactants and solvents are as described in the first method above. An acid/water mixture, as described above, is added to the reaction mixture while stirring. The resulting mixture is heated to about or above a temperature of 40°C and held at the desired temperature for 30 between approximately 1 and 24 hours to produce the absorbing material. The absorbing material is diluted and filtered as described above to form a coating solution. Again, as mentioned earlier, the at least one porogen, the at least one high-boiling solvent, the at least

one leveling agent, the at least one densifying agent, the at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof may be added during or after the first heating step.

5 . A method of forming an absorbing organohydridosiloxane material includes forming a mixture of a dual phase solvent which includes both a non-polar solvent and a polar solvent and a phase transfer catalyst; adding at least one organotrihalosilane, hydridotrihalosilane; adding at least one material modification agent, such as the at least one porogen, the at least one high-boiling solvent, the at least one leveling agent, the at least one densifying agent, the 10 at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof; and at least one absorbing compound, such as absorbing compounds 1 - 41, to provide a dual phase reaction mixture; and reacting the dual phase reaction mixture for between 1 and 24 hours to produce the absorbing organohydridosiloxane polymer. The phase 15 transfer catalyst includes but is not limited to tetrabutylammonium chloride and benzyltrimethylammonium chloride. Exemplary non-polar solvents include, but are not limited to, pentane, hexane, heptane, cyclohexane, benzene, toluene, xylene, halogenated solvents such as carbon tetrachloride and mixtures thereof. Useful polar solvents include water, alcohols, and alcohol and water mixtures. The absorbing polymer solution is diluted 20 and filtered as described above to form a coating solution.

In another embodiment, the catalyst may reside on a solid phase, with the polymerization proceeding on the surface. The support materials may include typical silica-based ion-exchange resins which have an attached acid group such as sulfonic acid, or any other acid-containing polymer (such as polylactide, polyacrylic acid, polyvinylsulfonic acid) 25 which is insoluble in the solvent conditions used.

In other embodiments, the water content of the composition during and after the synthesis and/or preparation of the absorbing coating composition can be controlled in order to control the molecular weight growth of the polymer. Controlling the water content has a similar effect as the capping agent to the polymer molecular weight growth.

30 Alternatively, yet another method of making an absorbing anti-reflective composition, requires at least one inorganic-based monomer to be added after the polymerization reaction

has started in a “staged silane addition” manner. Any remaining silane monomers, the incorporatable absorbing compound that absorbs light at wavelengths less than about 375 nm, and the at least one material modification agent, such as the at least one porogen, the at least one high-boiling solvent, the at least one leveling agent, the at least one densifying agent, the 5 at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof is then added to the reaction mixture.

APPLICATIONS

10 The absorbing coating solutions are applied to various substrates to form layered materials, layers used in semiconductor processing, or layers used in electronic components, depending on the specific fabrication process, typically by conventional spin-on deposition techniques. These techniques include a dispense spin, a thickness spin, and thermal bake steps, to produce an absorbing anti-reflective coating. Typical processes include a thickness spin of between 1000 and 4000 rpm for about 20 seconds and one to three bake steps at 15 temperatures between 80°C and 300°C for about one minute each. The absorbing anti-reflective coatings, according to the present invention exhibit refractive indices between about 1.3 and about 2.0 and extinction coefficients greater than approximately 0.07.

Substrates contemplated herein may comprise any desirable substantially solid 20 material. Particularly desirable substrate layers would comprise films, glass, ceramic, plastic, metal or coated metal, or composite material. In preferred embodiments, the substrate comprises a silicon or germanium arsenide die or wafer surface, a packaging surface such as found in a copper, silver, nickel or gold plated leadframe, a copper surface such as found in a circuit board or package interconnect trace, a via-wall or stiffener interface (“copper” includes 25 considerations of bare copper and its oxides), a polymer-based packaging or board interface such as found in a polyimide-based flex package, lead or other metal alloy solder ball surface, glass and polymers such as polyimide. In more preferred embodiments, the substrate comprises a material common in the packaging and circuit board industries such as silicon, copper, glass, and another polymer.

Contemplated coating materials, coating solutions and films can be utilized are useful in the fabrication of a variety of electronic devices, micro-electronic devices, particularly semiconductor integrated circuits and various layered materials for electronic and semiconductor components, including hardmask layers, dielectric layers, etch stop layers and 5 buried etch stop layers. These coating materials, coating solutions and films are quite compatible with other materials that might be used for layered materials and devices, such as adamantane-based compounds, diamantane-based compounds, silicon-core compounds, organic dielectrics, and nanoporous dielectrics. Compounds that are considerably compatible with the coating materials, coating solutions and films contemplated herein are disclosed in 10 PCT Application PCT/US01/32569 filed October 17, 2001; PCT Application PCT/US01/50812 filed December 31, 2001; US Application Serial No. 09/538276; US Application Serial No. 09/544504; US Application Serial No. 09/587851; US Patent 6,214,746; US Patent 6,171,687; US Patent 6,172,128; US Patent 6,156,812, US Application Serial No. 60/350187 filed January 15, 2002; and US 60/347195 filed January 8, 2002, which 15 are all incorporated herein by reference in their entirety.

A general method of using an absorbing material according to the present invention as an anti-reflective coating in a photolithographic process is illustrated in **Figures 2a-2h**. As shown in Fig. 2a, a dielectric layer 22 is deposited on a silicon substrate 20. Dielectric layer 22 can be composed of a variety of dielectric materials including, for example, a silicon 20 dioxide layer derived from TEOS, a silane based silicon dioxide layer, a thermally grown oxide, or a chemical-vapor-deposition-produced methylhydridosiloxane, OSG, FSG, NANOGLASS™-type of materials or silicon dioxide incorporating other elements or compounds. Dielectric layer 22 is typically an optically transparent medium, but it does not have to be an optically transparent medium. An absorbing anti-reflective coating layer 24 is 25 applied above dielectric layer 22 (Fig. 2b) that is covered by a photoresist layer 26, of a conventional positive photoresist, to produce the stack shown in Fig. 2c. The stack of Fig. 2c is exposed to ultraviolet radiation 32 through mask 30, as shown in Fig. 2d. During the exposure, the absorbing ARC layer 24 absorbs UV light 32 transmitted through the photoresist. Because the dielectric layer 22 is generally and usually transparent in the UV 30 wavelength range, if absorbing ARC layer 24 were not present, the UV light 32 would reflect off the underlying silicon layer 20, or other reflective surfaces such as poly silicon, copper, and high refractive index surfaces such as silicon nitride, etc., degrading a critical dimension,

for example critical dimension 27 of the exposed photoresist. In this example, a positive photoresist, which provides direct image transfer, is assumed. It should be appreciated, however, that some organic dielectrics are not optically transparent.

The exposed stack is developed to produce the stack of Fig. 2e. The absorbing ARC layer 24 is resistant to conventional photoresist developer solutions such as a 2.3% solution of tetramethylammoniumhydroxide (TMAH). In contrast, ARC layers, which have some of the chemical characteristics of the photoresist materials, are more sensitive to photoresist developers. Furthermore, it is anticipated that absorbing ARC layers are resistant to photoresist stripping processes, whereas organic ARC's are not resistant. Thus, use of absorbing layers may facilitate photoresist rework, without the need to reapply the ARC layer.

Next, a pattern is etched in the absorbing ARC layer 24 through the opening in photoresist layer 26 to produce the etched stack of Fig. 2f. A fluorocarbon etch, which has a high selectivity to photoresist, is used to etch the absorbing spin-on ARC layer 24. The response of the absorbing layer to a fluorocarbon etch provides an additional advantage of the absorbing layer over organic ARC layers, which require an oxygen plasma etch [RIE based plasma]. An oxygen plasma etch can degrade the critical dimension of the developed photoresist because the photoresist, being organic based, is also etched by an oxygen plasma. A fluorocarbon plasma consumes less photoresist than an oxygen plasma. At shorter UV wavelengths, depth of focus requirements will limit the thickness of photoresist layer 26 at the exposure step shown in Fig. 2d. For example, it is estimated that at 193 nm, the thickness of photoresist layer should be approximately 300 nm, and in several contemplated embodiments, thicknesses of about 250 nm are being used. Thus, as these short wavelengths start to be employed, it will be important to have an ARC layer that can be etched selectively with respect to the photoresist. Note the plasma etch rate selectivity of organic ARCs to photoresist rarely exceeds 2:1. Si-O based ARCs can show etch rate selectivities in excess of 6:1.

The fluorocarbon etch is continued through the dielectric layer 22 to produce the stack of Fig. 2g. Photoresist layer 26 is partially consumed during the continued etch process. Finally, the photoresist layer 26 is stripped using a suitable energy source, such as an oxygen plasma in some cases or a hydrogen reducing chemistry or via a wet chemistry and the ARC layer 24 is stripped using either a buffered oxide etch, for example a standard hydrofluoric

acid/water mixture, non, partially or complete aqueous fluoride chemistry, or an aqueous or non-aqueous organoamine. Advantageously, the ARC layer can be stripped with solutions that show a good selectivity with respect to the underlying dielectric layer. Thus, the general photolithographic method shown in Figs. 2a-2h illustrates the process advantages of 5 absorbing materials as anti-reflective coating layers and as sacrificial anti-reflective coating layers.

The compounds, coatings, films, materials and the like described herein may be used to become a part of, form part of or form an electronic component and/or semiconductor component. As used herein, the term "electronic component" also means any device or part 10 that can be used in a circuit to obtain some desired electrical action. Electronic components contemplated herein may be classified in many different ways, including classification into active components and passive components. Active components are electronic components capable of some dynamic function, such as amplification, oscillation, or signal control, which usually requires a power source for its operation. Examples are bipolar transistors, field-effect transistors, and integrated circuits. Passive components are electronic components that 15 are static in operation, i.e., are ordinarily incapable of amplification or oscillation, and usually require no power for their characteristic operation. Examples are conventional resistors, capacitors, inductors, diodes, rectifiers and fuses.

Electronic components contemplated herein may also be classified as conductors, 20 semiconductors, or insulators. Here, conductors are components that allow charge carriers (such as electrons) to move with ease among atoms as in an electric current. Examples of conductor components are circuit traces and vias comprising metals. Insulators are components where the function is substantially related to the ability of a material to be extremely resistant to conduction of current, such as a material employed to electrically 25 separate other components, while semiconductors are components having a function that is substantially related to the ability of a material to conduct current with a natural resistivity between conductors and insulators. Examples of semiconductor components are transistors, diodes, some lasers, rectifiers, thyristors and photosensors.

Electronic components contemplated herein may also be classified as power sources 30 or power consumers. Power source components are typically used to power other

components, and include batteries, capacitors, coils, and fuel cells. Power consuming components include resistors, transistors, integrated circuits (ICs), sensors, and the like.

Still further, electronic components contemplated herein may also be classified as discrete or integrated. Discrete components are devices that offer one particular electrical property concentrated at one place in a circuit. Examples are resistors, capacitors, diodes, and transistors. Integrated components are combinations of components that can provide multiple electrical properties at one place in a circuit. Examples are integrated circuits in which multiple components and connecting traces are combined to perform multiple or complex functions such as logic.

EXAMPLES**ANALYTICAL TEST METHODS:**

Shrinkage: Film shrinkage is measured by determining the film thickness before and after the process. Shrinkage is expressed in percent of the original film thickness. Shrinkage is positive 5 if the film thickness decreased. The actual thickness measurements are performed optically using a n&k Analyzer spectrophotometer.

Refractive Index: The refractive index (n) measurements are performed together with the thickness measurements using a n&k Analyzer spectrophotometer.

Absorption coefficient: The absorption coefficient (k) measurements are performed together 10 with the thickness measurements using a n&k Analyzer spectrophotometer.

Molecular Weight: The molecular weight (Mw) measurements are performed by using Gas Phase Chromatography.

Blanket Film Thickness: The blanket film thickness measurements are performed using an N&K Analyzer.

15 % Via Fill: The % Via Fill measurements are performed using a via-fill wafer along with a Scanning Electron Microscope.

Film Quality: The film quality measurements are performed using visual inspection along with a microscope.

20 The methods of synthesizing the absorbing materials comprising at least one inorganic-based material or composition and at least one material modification agent that includes at least one porogen, at least one high-boiling solvent, at least one capping agent, at least one leveling agent, at least one catalyst, at least one replacement solvent, at least one adhesion promoter, at least one pH tuning agent, and/or a combination thereof in order to couple with and improve the compatibility of a resist material, increase etch selectivity and/or stripping selectivity and increase planarizationability, while decreasing voiding are illustrated 25 in the following examples. The solutions and coatings prepared in the following examples are tuned and/or prepared in order to be compatible with several photoresist materials,

including those that absorb around 157 nm, 193 nm, 248 nm, and 375 nm. An example of the 193 nm resist material is an acrylate resist material.

EXAMPLE 1

5 In a 22-liter flask 6497.86 grams solvent, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 932.80 grams of butanol and 20650.0 g of ethyl lactate was added. The acetone alone or the 2-propanol/acetone mixture that would have 10 normally been used in the reaction is replaced with at least one replacement solvent. In one embodiment, a 2:1 mixture of ethanol/PGMEA is used as the at least one replacement solvent. In another embodiment, a 2:1 mixture of PGMEA/ethanol is used as the at least one replacement solvent. It is important to note that any of the compounds and/or mixtures found in Examples 6-21 can be substituted for the above-referenced compound. It is also important 15 to note that even though Examples 6-21 deal with absorbing compounds and pH tuning agent addition, the pH tuning agent may be included or excluded along with the acetone-free situation described in this Example, in order to produce an absorbing composition such as those described herein.

20 **Table 1** shows a preliminary aging study using the acetone-free and acetone/IPA-free mixtures. In Table 1, "POR" stands for the control, which used both acetone and IPA as solvents.

Figures 3-14 show the graphical representations of the preliminary aging data found 25 in Table 1, including molecular weights, thickness, polydispersity and pH stability over a 7 day period of time.

Table 2 shows the reflux time, temperature, gas chromatography information, thickness, optical properties, ratios of water, ethanol, butanol and PGMEA, density, pH and total percent solids for 6 "runs" of the above-referenced material. **Table 3** shows the heat ramp data for those 6 runs (each run having a specific "Run ID" meaning a particular reflux time v. reflux temperature), and **Figure 15** shows the graphical representations of the time v. 30 temperature for those 6 runs. The heat ramp experiments are designed to show how well the

materials respond to applied heat. The temperature of the material is measured at specific time intervals as a constant heat is applied.

EXAMPLE 2

5 In a 22-liter flask 6331.20 grams 2-propanol, 3166.66 grams solvent, such as acetone, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 932.80 grams of butanol and 20650.0 g of ethyl lactate was added. The material modification agent 10 added for this set of examples was the at least one high boiling solvent, which was in this case glycerol. For this set of experimental data, 1% glycerol was added to the mixture to eliminate voiding and to improve the % via fill in the absorbing composition coating material. It is important to note that any of the compounds and/or mixtures found in Examples 6-21 can 15 be substituted for the above-referenced compound. It is also important to note that even though Examples 6-21 deal with absorbing compounds and pH tuning agent addition, the pH tuning agent may be included or excluded along with the high boiling point solvent situation described in this Example, in order to produce an absorbing composition such as those described herein.

20 **Table 4 (parts 1 and 2)** shows the summary of the via fill versus the thickness and pitch for control materials at different pH measurements versus the control materials plus the high boiling point solvents at different pH measurements. **Figures 16-27** show the graphical representation of the data and resulting trends regarding blanket film thickness and % fill in 25 **Table 4 (parts 1 and 2)**. **Figure 28** shows the actual SEM data for a wafer with absorbing composition and a wafer with absorbing composition that further comprises a high boiling point solvent.

EXAMPLE 3

In a 22-liter flask 6331.20 grams 2-propanol, 3166.66 grams acetone, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 30 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The

flask was refluxed and/or heated for 1 to 12 hours. The heating/refluxing time was divided into four relatively equal time intervals, and at each time interval TMEOS was added in 0.2g, 0.5g, 1g and 5g amounts respectively. To the solution, 20650.0 g of ethyl lactate was added. Also, in some of the embodiments 932.80 grams of butanol was added after the TMEOS 5 addition was completed. The material modification agent added for this set of examples was the at least one capping agent, which was in this case TMEOS. It is important to note that any of the compounds and/or mixtures found in Examples 6-21 can be substituted for the above-referenced compound. It is also important to note that even though Examples 6-21 deal with absorbing compounds and pH tuning agent addition, the pH tuning agent may be 10 included or excluded along with the high boiling point solvent situation described in this Example, in order to produce an absorbing composition such as those described herein.

The parents were aged for one week at 40°C. For the aged parent, time of addition of TMEOS was not significant to polymer molecular weight growth. The polymer molecular weight growth was smallest for the three aged parents where 5g of TMEOS were added. For 15 the three parents where 5g of TMEOS were added (3hrs into reflux, before butanol, after butanol), the GC showed a peak for TMEOS, except for the parent where TMEOS was added three hours into reflux. Five samples with the smallest polymer molecular weight growth slope were chosen as possible candidates. The parents chosen were all three samples with 5 g 20 of TMEOS added, one sample with 1g of TMEOS added 3 hrs into reflux, and one sample with 1g of TMEOS added instead of butanol. The five parents were diluted to form the absorbing coating composition and aged for 1 week at 40°C. For the aged child, the polymer molecular weight growth was smallest for the three children where 5 g of TMEOS were added.

The polymer molecular weight growth may also be controlled and/or stopped by 25 controlling the water content of the parent formulation, since a majority of the polymer molecular weight growth occurs upon dilution, regardless of the parent molecular weight. In some embodiments, the water was reduced by about 20%. **Table 5** and **Table 6** show the Parent and Child QC results from the water controlling experiments. **Figures 29 and 30** show a graphical representation of the water controlling experiment data based on molecular 30 weight versus time (hours).

EXAMPLE 4

In a 22-liter flask 6331.20 grams 2-propanol, 3166.66 grams solvent, such as acetone, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were 5 combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 20650.0 g of ethyl lactate and 932.80 grams of butanol was added. The material modification agent added for this set of examples was either one specific agent, such as a replacement solvent or a combination of several agents, such as at least one leveling agent and at least one replacement solvent. It is important to note that any of the compounds and/or mixtures found 10 in Examples 6-21 can be substituted for the above-referenced compound. It is also important to note that even though Examples 6-21 deal with absorbing compounds and pH tuning agent addition, the pH tuning agent may be included or excluded along with the high boiling point solvent situation described in this Example, in order to produce an absorbing composition such as those described herein. **Table 7** shows the data collected for this example and **Figure 15** 31 shows a graphical representation of some of this data – the delta thickness (isolated-dense).

In another related example, the viscosity of the absorbing composition was modified by the following procedure. The above-prepared absorbing composition that comprised a replacement solvent and no acetone was spun-on to a substrate at 2000RPM a thickness of 20 3000Å with BYK 306 surfactant present. About 2 grams of leveling and viscosity agents BYK 410, 420, 380 and/or 381 may be added. The surfactant may or may not be present in additional examples when the leveling and/or viscosity agents are added. The additive may be added to a child (already diluted like in the example above), they may be diluted further after the additive is added or not. Or the additive may be added to a parent and then either 25 diluted or not. There may be only one additive added or we might combine the additives using more than one on a sample to get the combined effects. A range of dilution factors were used for 410, 420, 380, and 381 to test the effect on the properties. The main effect that we were looking for was via fill, as these samples were spun up on patterned wafers and looked at under the SEM.

30 For the data related to surfactants, the following summary applies:

SURFACTANTS TESTED

	FC-4430	(3M)
	FC-4432	(3M)
	L-18459	(3M)
5	Brij-30	(Aldrich)
	Brij-35	(Aldrich)
	Brij-58	(Aldrich)
	Brij-72	(Aldrich)
	Brij-76	(Aldrich)
10	Brij-78	(Aldrich)
	Brij-98	(Aldrich)
	Brij-700	(Aldrich)
	PolycarboMethylSilane	(Aldrich)
	Tergitol TMN -6	(Dow)
15	Tergitol minifoam 2x	(Dow)
	Tagopren-6870D	(Goldschmit)
	Tagopren-5843	(Goldschmit)
	Tagopren-5852	(Goldschmit)
	Tagopren-6871	(Goldschmit)
20	Tagopren-7008	(Goldschmit)
	Tagopren-5884	(Goldschmit)
	Tagopren-5863	(Goldschmit)
	Tagopren-5851	(Goldschmit)
	Tagopren-5857	(Goldschmit)
25	Tagopren-5040	(Goldschmit)
	Clarian surfactant	(Clarian)
	BYK 306	(BYK Chemie)
	BYK 307	(BYK Chemie)
	BYK 320	(BYK Chemie)
30	BYK 333	(BYK Chemie)

At this time, several of the above-listed surfactants are successfully being utilized to eliminate striations at various loading points. Data and observations for several of the surfactants utilized are presented below; however, these data and observations are not

exhaustive of the studies conducted and do not represent all of the surfactants tested. For example, the following classes of surfactants were tested: polyacrylates (both ionic and non-ionic) (BYK brand surfactants), functional polydimethylsiloxanes (Tagopren brand surfactants), silicones, fluorinated alkylesters (FC brand surfactants), polyether and aliphatic hydrocarbon chain surfactants (Brij surfactants).

FC-4430

Five 200mm samples were made with the loading range of 0.007 to 0.116 of FC-4430, and all were tested before and after filtration and the highest three loading were sent to 10 Sunnyvale for testing on 8" wafers. All loadings had striations before and after filtration.

FC-4430 was then tested on 300mm material loading range of 0.004 to 0.019. The striations were seen to decrease in severity as the loading increased with some wafers of loading 0.019 having no visible striations and other having visible striations.

FC-4430 300mm samples with surfactant loading 0.015, 0.019, 0.023 at multiple spin 15 speeds. There were striations seen on 0.015 and 0.019 loading wafers and some of the 0.023 loading wafers had visible striations and others didn't.

FC-4432

FC-4432 in 200mm Sample loading 0.004 to 0.2, sample loading 0.08 and 0.1 had no 20 striations visible so samples were sent to Sunnyvale along with std 200mm material to be spun on 8" wafers and similarly no striations were visible, dewetting was noticeable on 0.1 loading sample. No filtration was done to eliminate and filtration interactions.

FC-4432 was tested in 200mm and 300mm in loadings from 0.004 to 0.11 in small increments to determine the lowest concentration that the FC-4432 worked to eliminate 25 striations. The loading was found to be 0.005 in 300mm and 0.04 in 200mm. No filtration was done to eliminate filtration interactions.

FC-4432 the samples loadings that worked in the previous samples were repeated with larger sample sizes and half was filtered and half was unfiltered. 200mm material had

loading 0.03 to 0.06. 300mm had loadings of 0.04 to 0.06. The filtered samples required a slightly higher surfactant loading than the unfiltered to eliminate striations.

Tagopren 5884

5 Tagopren 5884 was tested in 300mm with loadings of 0.006 to 0.11. None of the wafers had striations however there was a large thickness variation around the edge of the wafer.

10 Tagopren 5884 was mixed with other surfactants that did not have a large edge thickness variation, Tagopren 5851 and 5857 and FC-4430, to determine if mixing could create no striations and no edge thickness variation. The edge thickness variation was not eliminated.

Tagopren 5884 was used in the same loading that worked in earlier experiments (Loading 0.004, 0.006, and 0.008). The samples were made and filtered, none had striations.

15 **Tagopren 5863**

Tagopren 5863 was tested in 300mm with loadings of 0.006 to 0.11. Samples with a loading of 0.015 or higher did not show striations, samples with a loading lower than 0.015 did have striations. There was a large thickness variation around the edge of the wafer.

20 Tagopren 5863 was mixed with other surfactants that did not have a large edge thickness variation, Tagopren 5851 and 5857, to determine if mixing could create no striations and no edge thickness variation. The edge thickness variation was not eliminated.

Tagopren 5863 was used in the same loading that worked in earlier experiments (Loading 0.015, 0.017, and 0.019). The sample with loading 0.019 did not have striations, the 0.015 and 0.017 had a few striations however did not show the striation pattern.

Tagopren 5851, and 5857

Tagopren 5851 and 5857 were tested in 300mm with loadings of 0.006 to 0.11. All wafers spun had visible striations. There was not a large thickness variation around the edge of the wafer.

5 Tagopren 5851 and 5857 were mixed with other surfactants that did not have striations to see if these surfactants would eliminate the edge thickness variation seen in other Tagopren samples to determine if mixing could create no striations and no edge thickness variation. Edge thickness variation was visible on the mixed surfactant samples.

10

L-18459

This sample was tested in a 10% solution of EL and tested at loadings of 0.003 to 0.02 and wafers at loadings of 0.005 and above showed no striations.

15

EXAMPLE 5

One of the best ways to improve the etching selectivity and/or stripping selectivity of the absorbing composition, as mentioned earlier, is increasing the surface area through the addition of a porogen to the material and then creating pores after the application of energy.

20 In a 22-liter flask 6331.20 grams 2-propanol, 3166.66 grams acetone, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 20650.0 g of ethyl lactate and 932.80 grams of butanol was added. The material modification agent added for this set of examples was at least one porogen, such as poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPO). It is important to note that any of the compounds and/or mixtures found in

Examples 6-21 can be substituted for the above-referenced compound. It is also important to note that even though Examples 6-21 deal with absorbing compounds and pH tuning agent addition, the pH tuning agent may be included or excluded along with the high boiling point solvent situation described in this Example, in order to produce an absorbing composition such as those described herein. Table 8 shows a set of experiments conducted using the absorbing compound in this example. Again, it should be noted that any one of the absorbing compositions can be substituted in these experiments. In Table 8, the following abbreviations are used: PEO = poly(ethylene oxide); TMAA = tetramethylammonium acetate; TMAH = etching solution at 2.3% and 23°C.

10

Table 8:

Added to 248 nm absorbing compound	PEO Loading	TMAA Loading	Bake Temps (°C)	Pre-TMAH Dip	Error	Thickness After (Angstrom s)	Error	Change in Thickness
Control	0	0	130/250/300	1306.11	8.077	1323.22	5.544	17.11
0.025 PEO	0.025	0	130/250/300	1337.9	3.966	1320.23	5.943	-17.67
	0.025	0	130/200/250	1387.44	6.154	1313.27	6.501	-74.17
0.025PEO 0.0004 TMAA	0.025	0.0004	130/250/300	1443.24	5.109	1433.17	11.474	-10.07
	0.025	0.0004	130/200/250	1453.95	6.319	1451.52	4.405	-2.43
	0.025	0.0004	130/250/300	1444.83	3.722	1430.99	7.652	-13.84
	0.025	0.0004	130/200/250	1447.68	11.305	1520.1	5.492	72042
0.025 PEO 0.0008 TMAA	0.025	0.0008	130/250/300	1449.61	5.359	1439.04	7.335	-10.57
	0.025	0.0008	130/200/250	1459.76	4.681	1460.35	5.609	0.59
0.025 PEO 0.0012 TMAA	0.025	0.0012	130/250/300	1449.66	3.589	1445.21	9.189	-4.45
	0.025	0.0012	130/200/250	1453.16	8.004	1461.43	4.365	8.27
	0.025	0.0012	130/250/300	1450.41	4.333	1444.04	8.872	-6.37
	0.025	0.0012	130/200/250	1464.64	6.23	1452.44	5.895	-12.2
0.01 PEO	0.01	0	130/250/300	1420.51	4.607	1350.19	5.369	-70.32
	0.01	0	130/200/250	1500.26	4.078	1501.14	4.926	0.88
0.01 PEO 0.0004 TMAA	0.01	0.0004	130/250/300	1566.8	5.655	1465.9	8.667	-100.9
	0.01	0.0004	130/200/250	1590.99	5.982	44.32	78.299	-1546.67
0.01 PEO 0.0008 TMAA	0.01	0.0008	130/250/300	1584.02	5.874	1488.89	8.474	-95.13
	0.01	0.0008	130/200/250	1601.38	5.655	1479.67	4.406	-121.71
0.01 PEO 0.0012 TMAA	0.01	0.0012	130/250/300	1588.45	6.463	1495.91	8.531	-92.54

	0.01	0.0012	130/200/250	1608.47	6.685	1504.56	5.171	-103.91
0.05 PEO	0.05	0	130/250/300	1375.22	8.297	1341.01	6.316	-34.21
	0.05	0	130/200/250	1426.35	7.529	1293.13	7.829	-133.22
0.05 PEO 0.0004 TMAA	0.05	0.0004	130/250/300	1492.67	6.268	1463.57	10.238	-29.1
	0.05	0.0004	130/200/250	1508.78	4.395	1293.13	7.829	-215.65
	0.05	0.0004	130/250/300	1491.96	6.696	1460.68	8.451	-31.28
	0.05	0.0004	130/200/250	1514.64	5.787	1488.56	8.167	-26.08
0.05 PEO 0.0008 TMAA	0.05	0.0008	130/250/300	1502.61	5.237	1475.98	6.47	-26.63
	0.05	0.0008	130/200/250	1515.99	4.985	1483.06	3.413	-32.93
0.05 PEO 0.0012 TMAA	0.05	0.0012	130/250/300	1503.28	5.771	1475.95	6.665	-27.33
	0.05	0.0012	130/200/250	1516.91	4.53	1495.9	3.86	-21.01
	0.05	0.0012	130/250/300	1498.59	6.526	1472.97	8.438	-25.62
	0.05	0.0012	130/200/250	1522.47	7.068	1505.01	6.411	-17.46

EXAMPLE 6

Synthesis of an absorbing material containing 9-anthracene carboxy-methyl triethoxysilane and a pH tuning agent

In a 22-liter flask 6331.20 grams 2-propanol, 3166.66 grams acetone, 2633.78 grams TEOS, 1639.78 grams MTEOS, 958.97 grams 9-anthracene carboxy-methyl triethoxysilane, 119.24 grams 0.1 M nitric acid and 1425.58 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 932.80 grams of butanol and 20650.0 g of ethyl lactate was added. The solution was filtered to be used in the pH tuning experiments. A pH tuning agent, 0.1 M nitric acid, was added to 2 separate solutions of 650 g of the spin-on material that has a starting pH of about 1.5. The nitric acid was added in the following amounts and gave the following pH: a) 2.794 g (pH = 0.7); b) 0.293 g (pH = 0.75). APTEOS was added to two additional and separate solutions of 650 g of the same spin-on material in the following amounts giving the following pH values: a) 0.053 g (pH = 4.13); b) 0.151 g (pH = 5.47). The solutions were then dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1402.17 Å. At 248 nm, the refractive index (n) was 1.47 and the

extinction coefficient (k) was 0.429. The same spin and bake process parameters and measurement technique was used in all of the following examples.

5

**Synthesis of another absorbing material containing
9-anthracene carboxy-methyl triethoxysilane and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M 10 nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245

grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology 5 Model 1200 analyzer. The film thickness was 1635 Å. At 248 nm, the refractive index (n) was 1.373 and the extinction coefficient (k) was 0.268. It should be appreciated, however, that the refractive index and extinction coefficient data for this example and all of the following and contemplated examples could change depending on the purity of the initial reactants and starting compounds. The same spin and bake process parameters and 10 measurement technique was used in all of the following examples.

Synthesis of absorbing material containing

9-anthracene carboxy-methyl triethoxysilane and pH tuning agent

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.01 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 20 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å. At 248 nm, the refractive index (n) was 1.373 and the extinction coefficient (k) was 0.268.

25

Synthesis of absorbing material containing

9-anthracene carboxy-methyl triethoxysilane and pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 30 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 1.0 M

nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was 5 dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å.

Synthesis of absorbing material containing

10 9-anthracene carboxy-methyl triethoxysilane and pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 100 grams deionized water were combined. The flask was refluxed and/or 15 heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology 20 Model 1200 analyzer. The film thickness was 1635 Å.

Synthesis of absorbing material containing

9-anthracene carboxy-methyl triethoxysilane and pH tuning agent

25 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 130 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 30 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was

dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å.

5

**Synthesis of absorbing material containing
9-anthracene carboxy-methyl triethoxysilane and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 77 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 1 g of APTEOS was added to the solution during refluxing. After refluxing, to the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å. At 248 nm, the refractive index (n) was 1.373 and the extinction coefficient (k) was 0.268.

20

**Synthesis of absorbing material containing
9-anthracene carboxy-methyl triethoxysilane and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M nitric acid and 77 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 1 g of APTEOS was added to the solution after refluxing. Also after refluxing, to the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for

one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. The film thickness was 1635 Å.

Synthesis of absorbing material containing

5 9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 10 M acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 10 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 15 analyzer.

Synthesis of absorbing material containing

9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent

20 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 1.0 M acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, 25 Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams pure acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, 10 followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 10 M acetic acid and 100 grams deionized water were combined. The flask was refluxed and/or heated 20 for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for 25 one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77
5 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 1.0 M acetic
acid and 130 grams deionized water were combined. The flask was refluxed and/or heated
for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of
acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,
10 Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for
one minute each. Optical properties were measured with an N & K Technology Model 1200
analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77
grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams pure acetic
acid and 72 grams deionized water were combined. 1.0 g of potassium hydroxide was added
20 before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution,
115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53
grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added.
The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness
spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties
25 were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77
5 grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 10 M acetic
acid and 72 grams deionized water were combined. 1.0 g of potassium hydroxide was added
during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution,
115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53
grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added.
10 The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness
spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties
were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77
grams MTEOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 1.0 M acetic
acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for
20 1 to 12 hours. 1.0 g of potassium hydroxide was added before refluxing. Also, to the
solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of
ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN)
were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm
thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical
25 properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams
5 MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams pure lactic acid
and 40 grams deionized water were combined. The flask was refluxed and/or heated for 1 to
12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone,
329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,
10 Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for
one minute each. Optical properties were measured with an N & K Technology Model 1200
analyzer. Thickness is 1487.1 Angstroms; $k = 0.4315$; $n=1.4986$.

**Synthesis of absorbing material containing
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams
MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid
and 40 grams deionized water were combined. The flask was refluxed and/or heated for 1 to
12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone,
329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,
20 Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for
one minute each. Optical properties were measured with an N & K Technology Model 1200
25 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams
5 MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams pure lactic acid
and 40 grams deionized water were combined. The flask was refluxed and/or heated for 1 to
12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone,
329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,
10 Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for
one minute each. Optical properties were measured with an N & K Technology Model 1200
analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams
MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 1.0 M lactic acid
and 70 grams deionized water were combined. The flask was refluxed and/or heated for 1 to
20 12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone,
329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,
Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for
one minute each. Optical properties were measured with an N & K Technology Model 1200
25 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams
5 MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid
and 90 grams deionized water were combined. The flask was refluxed and/or heated for 1 to
12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone,
329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,
10 Minneapolis, MN) were added. The solution was filtered. The solution was dispensed,
followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for
one minute each. Optical properties were measured with an N & K Technology Model 1200
analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams
MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid
and 40 grams deionized water were combined. 1.5 g of TMAH was added to the solution
20 before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 26
grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53
grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added.
The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness
spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties
25 were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid and 40 grams deionized water were combined. 1.5 g of TMAH was added to the solution during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

10 The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid and 40 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 1.5 g of TMAH was added to the solution after refluxing. Also after refluxing, to the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer.

**Synthesis of absorbing material containing
9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 178 grams 2-propanol, 89 grams acetone, 52 grams TEOS, 59 grams 5 MTEOS, 29 grams 9-anthracene carboxy-propyl triethoxysilane, 3.3 grams 10 M lactic acid and 40 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 26 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) were added. The solution was filtered. The solution was dispensed, 10 followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. Thickness is 1487.1 Angstroms; k = 0.4315; n=1.4986.

EXAMPLE 7

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

5

10 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, 15 Minneapolis, MN) were added. Thickness= 1436 Å, n= 1.479, k = 0.1255.

15

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

20

25 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.01 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

30

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 1.0 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 10 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 95 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

25 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-

triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 110 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, 5 Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

10

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. 1.2 g of APTEOS was added to the solution 15 before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. 1.2 g of APTEOS was added to the solution 25 during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

30

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 25 grams 9-anthracene methanol, 10 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 1.2 g of APTEOS was added to the solution after refluxing. Also, after refluxing, to 10 the solution, 111 grams of butanol, 459 grams 2-propanol, 230 grams of acetone, 309 grams of ethanol, 50 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

EXAMPLE 8

15

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

20 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 10 M acetic acid and 71.90 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To 25 the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-
diphenylketone, 5 grams rosolic acid, 0.5599 grams 1.0 M acetic acid and 71.90 grams
deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of
10 ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)
were added.

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-
diphenylketone, 5 grams rosolic acid, 0.5599 grams pure acetic acid and 71.90 grams
20 deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of
ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)
were added.

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

25 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-
diphenylketone, 5 grams rosolic acid, 0.5599 grams 10 M acetic acid and 95 grams deionized

water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

5

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

10 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 10 M acetic acid and 120 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

15

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

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25

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 10 M acetic acid and 71.90 grams deionized water were combined. 2.2 g of potassium hydroxide was added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-
diphenylketone, 5 grams rosolic acid, 0.5599 grams 10 M acetic acid and 71.90 grams
deionized water were combined. 2.2 g of potassium hydroxide was added to the solution
during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57
10 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams
deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

15 **Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and a pH tuning
agent**

 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 93 grams TEOS, 77 grams
MTEOS, 20 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-
diphenylketone, 5 grams rosolic acid, 0.5599 grams 1075M acetic acid and 71.90 grams
20 deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 2.2
g of potassium hydroxide was added to the solution after refluxing. Also, after refluxing, to
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of
ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)
were added.

EXAMPLE 9

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 10 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4275 Å, n= 1.529, k = 0.124.

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.01 M nitric acid 20 and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4275 Å, n= 1.529, k = 0.124.

25

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77
grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 1.0 M nitric acid
and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to
12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone,
59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M,
10 Minneapolis, MN) were added. Thickness= 4275 Å, n= 1.529, k = 0.124.

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77
grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid
and 95 grams deionized water were combined. The flask was refluxed and/or heated for 1 to
12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone,
20 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M,
Minneapolis, MN) were added. Thickness= 4275 Å, n= 1.529, k = 0.124.

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

25

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77
grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-
triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid
and 125 grams deionized water were combined. The flask was refluxed and/or heated for 1 to

12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4275 Å, n= 1.529, k = 0.124.

5

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid and 72 grams deionized water were combined. 3 g of APTEOS was added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4275 Å, n= 1.529, k = 0.124.

15

**Synthesis of absorbing SOG containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, and pH tuning agent**

20

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid and 72 grams deionized water were combined. 3 g of APTEOS was added to the solution during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4275 Å, n= 1.529, k = 0.124.

25

Synthesis of absorbing SOG containing 9-anthracene methanol, 2-hydroxy-4-(3-triethoxysilyloxy)-diphenylketone, rosolic acid, and pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 108 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 5 grams rosolic acid, 0.5599 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 3 g of APTEOS was added to the solution after refluxing. Also, after refluxing, to the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 4275 Å, n= 1.529, k = 0.124.

EXAMPLE 10

15 **Synthesis of absorbing material containing
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3592 Å, $n=1.563$, $k=0.067$.

25 **Synthesis of absorbing material containing
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams 0.01 M nitric acid and 72 grams deionized water were combined. The flask was refluxed

and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

5

**Synthesis of absorbing material containing
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams 10 1.0 M nitric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

15

**Synthesis of absorbing material containing
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams 20 0.1 M nitric acid and 90 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

25

**Synthesis of absorbing material containing
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51
5 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams
0.1 M nitric acid and 125 grams deionized water were combined. The flask was refluxed
and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol,
44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10%
4FC 430 (3M, Minneapolis, MN) were added.

10

**Synthesis of absorbing material containing
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51
15 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams
0.1 M nitric acid and 72 grams deionized water were combined. 0.26 g of APTEOS was
added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12
hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59
grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M,
20 Minneapolis, MN) were added.

**Synthesis of absorbing material containing
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

25 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51
grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams
0.1 M nitric acid and 72 grams deionized water were combined. 0.26 g of APTEOS was
added to the solution during the refluxing step. The flask was refluxed and/or heated for 1 to
12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone,

59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

5 **Synthesis of absorbing material containing
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 0.6 grams 0.1 M nitric acid and 72 grams deionized water were combined. The flask was refluxed 10 and/or heated for 1 to 12 hours. 0.26 g of APTEOS was added to the solution after refluxing. Also, after refluxing, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added to the solution.

15 **Synthesis of absorbing material containing
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams 20 10 M lactic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51
5 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams
1.0 M lactic acid and 72 grams deionized water were combined. The flask was refluxed
and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol,
44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10%
FC 430 (3M, Minneapolis, MN) were added.

10

**Synthesis of absorbing material containing
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51
15 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams
1.0 M lactic acid and 72 grams deionized water were combined. The flask was refluxed
and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol,
44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10%
FC 430 (3M, Minneapolis, MN) were added.

20

**Synthesis of absorbing material containing
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51
25 grams MTEOS, 75 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams
10 M lactic acid and 72 grams deionized water were combined. The flask was refluxed
and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol,
44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10%
FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams 10 M lactic acid and 115 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10%
10 FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams 10 M lactic acid and 72 grams deionized water were combined. 0.06 g of APTEOS was added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN),
20 were added.

**Synthesis of absorbing material containing
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams 10 M lactic acid and 72 grams deionized water were combined. 0.06 g of APTEOS was added to the solution during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) 10 were added.

**Synthesis of absorbing material containing
2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone and a pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51 grams MTEOS, 60 grams 2-hydroxy-4-(3-trimethoxysilypropoxy)-diphenylketone, 0.6 grams 10 M lactic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 0.06 g of APTEOS was added to the solution after refluxing. After refluxing, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of 20 ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were also added to the solution.

EXAMPLE 11**Synthesis of absorbing material containing 9-anthracene methanol
and a pH tuning agent**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol
and a pH tuning agent**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.01 M hydrochloric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol
and a pH tuning agent**

25

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 1.0 M hydrochloric acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59

grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

Synthesis of absorbing material containing 9-anthracene methanol and a pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 100 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

Synthesis of absorbing material containing 9-anthracene methanol and a pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 130 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol
and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77
grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 72
grams deionized water were combined. 1.2 g of potassium hydroxide was added to the
solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the
solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of
ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)
10 were added.

**Synthesis of absorbing material containing 9-anthracene methanol
and a pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77
grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 72
grams deionized water were combined. 1.2 g of potassium hydroxide was added to the
solution during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the
solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of
20 ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)
were added.

**Synthesis of absorbing material containing 9-anthracene methanol
and a pH tuning agent**

25

 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77
grams MTEOS, 10 grams 9-anthracene methanol, 0.6 grams 0.1 M hydrochloric acid and 72
grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12
hours. 1.2 g of potassium hydroxide was added to the solution after refluxing. Also after

refluxing, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added to the solution.

5

EXAMPLE 12

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

10

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 1.0 M acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To 15 the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3503 Å, n= 1.475, k = 0.193.

20

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

25

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams pure M acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

10

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

15

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 98 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

20

25

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 120 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

10

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 72 grams deionized water were combined. 1.5 g of TMAH was added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

20

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 72 grams deionized water were combined. 1.5 g of TMAH was added to the solution during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 10 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

15 **Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

20 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M acetic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 1.5 g of TMAH was added to the solution after refluxing. Also after refluxing, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added to the solution.

EXAMPLE 13

5 **Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol; 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3119 Å, $n = 1.454$, $k = 0.175$.

15

Synthesis of absorbing material containing 9-anthracene methanol, 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid and a pH tuning agent

20 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77
grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of
9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 1.0 M lactic acid and 72 grams
deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To
the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of
ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN)
25 were added.

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams pure lactic acid and 72 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) 10 were added.

15 **Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 100 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 20 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 130 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, 10 Minneapolis, MN) were added.

15 **Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

20 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 72 grams deionized water were combined. 0.1 g of APTEOS was added to the solution before refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

**Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

5 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 72 grams deionized water were combined. 0.1 g of APTEOS was added to the solution during refluxing. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams 10 10 of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

15 **Synthesis of absorbing material containing 9-anthracene methanol,
2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid
and a pH tuning agent**

15 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid, 0.6 grams 10 M lactic acid and 72 grams 20 deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. 0.1 g of APTEOS was added to the solution after refluxing. Also after refluxing, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added to the solution.

EXAMPLE 14

Synthesis of absorbing material containing 9-anthracene methanol, 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, quinizarin, alizarin and a pH tuning agent

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 20 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, and 5 grams of rosolic acid; 2 grams of quinizarin, 2 grams alizarin, 10 0.6 grams 0.1 M nitric acid, 1.0 M nitric acid and 0.01 M nitric acid (added to three separate mixtures) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams 15 of 10% FC 430 (3M, Minneapolis, MN) were added. Thickness= 3554 Å, $n= 1.489$, $k= 0.193$.

In three additional solutions, 1.1 g of potassium hydroxide was added. In each solution, the potassium hydroxide was added before, during and after the refluxing step, respectively.

20

EXAMPLE 15

Synthesis of absorbing material containing 9-anthracene methanol, 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, rosolic acid, alizarin and a pH tuning agent

25

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 51.5 grams MTEOS, 5 grams 2-hydroxy-4-(3-triethoxysilypropoxy)-diphenylketone, 25 grams of 9-anthracene methanol, 5 grams of rosolic acid, and 2 grams alizarin, 0.5599 grams 1.0 M, 10

M and pure acetic acid (added to three separate mixtures, respectively) and 71.90 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 56.68 grams of butanol, 87.99 grams 2-propanol, 44.10 grams 5 of acetone, 59.31 grams of ethanol, 9.55 grams deionized water and 3.75 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 0.25 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

10

EXAMPLE 16**Synthesis of absorbing material containing 9-anthracene carboxy-methyl triethoxysilane and a pH tuning agent**

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In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 30 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 0.1 M, 0.01 M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 20 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10 % FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 0.25 g of HCl was added. In each solution, the HCl was added before, during and after the refluxing step, respectively.

25

Synthesis of absorbing material containing 9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 30 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 1.0 M, 10 M and pure lactic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 1.2 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

15 **Synthesis of absorbing material containing 9-anthracene
carboxy-propyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 30 grams 9-anthracene carboxy-propyl triethoxysilane, 0.6 grams 1.0 M, 10 M and pure lactic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 0.2 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

Synthesis of absorbing material containing 9-anthracene carboxy-pentyl triethoxysilane and a pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77
5 grams MTEOS, 30 grams 9-anthracene carboxy-pentyl triethoxysilane, 0.6 grams 0.1 M, 0.01
M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams
deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and
110 g of deionized water were added, respectively. The flask was refluxed and/or heated for
1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of
10 acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M,
Minneapolis, MN) were added.

In three additional solutions, 1.0 g of potassium hydroxide was added. In each
solution, the potassium hydroxide was added before, during and after the refluxing step,
respectively.

15

Synthesis of absorbing material containing 9-anthracene carboxy-methyl trimethoxysilane and a pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77
20 grams MTEOS, 30 grams 9-anthracene carboxy-methyl trimethoxysilane, 0.6 grams 1.0 M,
10 M and pure acetic acid (added to three separate solutions, respectively) and 72 grams
deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and
110 g of deionized water were added, respectively. The flask was refluxed and/or heated for
1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of
25 acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M,
Minneapolis, MN) were added.

In three additional solutions, 2.4 g of TMAH was added. In each solution, the TMAH
was added before, during and after the refluxing step, respectively.

Synthesis of absorbing material containing 9-anthracene carboxy-ethyl trimethoxysilane and a pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 30 grams 9-anthracene carboxy-ethyl trimethoxysilane, 0.6 grams 1.0 M, 10 M and pure lactic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 1.2 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

15 **Synthesis of absorbing material containing 9-anthracene
carboxy-propyl trimethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, 30 grams 9-anthracene carboxy-propyl trimethoxysilane, 0.6 grams 0.1 M, 20 0.01 M and 1.0 M hydrochloric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M hydrochloric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% 25 FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 1.4 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

EXAMPLE 17**Synthesis of absorbing material containing 9-anthracene methanol
and a pH tuning agent**

5

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, and 10 grams 9-anthracene methanol are combined. The solution is refluxed for 6 hours. A mixture of 0.6 grams 0.1 M, 0.01 M and 1.0 M hydrochloric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M hydrochloric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 1.4 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing 9-anthracene ethanol
and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, and 10 grams 9-anthracene ethanol are combined. The solution is refluxed for 6 hours. A mixture of 0.6 grams 0.1 M, 0.01 M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

In three additional solutions, 0.4 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

Synthesis of absorbing material containing 9-anthracene propanol

5 **and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 123 grams TEOS, 77 grams MTEOS, and 10 grams 9-anthracene propanol are combined. The solution is refluxed for 6 hours. A mixture of 0.6 grams 1.0 M, 10 M and pure acetic acid (added to three 10 separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams of butanol, 88 grams 2-propanol, 44 grams of acetone, 59 grams of ethanol, 9.5 grams deionized water and 3.7 grams of 10% FC 430 (3M, Minneapolis, MN) were added.

15 In three additional solutions, 1.25 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

EXAMPLE 18

20 **Synthesis of absorbing material containing 9-anthracene
carboxy-methyl triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59 grams MTMOS, 60 grams 9-anthracene carboxy-methyl triethoxysilane, 0.6 grams 1.0 M, 10 25 M and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask is refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of

acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

In three additional solutions, 1.25 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

5

Synthesis of absorbing material containing 9-anthracene carboxy-ethyl triethoxysilane and a pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59
10 grams MTMOS, 60 grams 9-anthracene carboxy-ethyl triethoxysilane, 0.6 grams 0.1 M, 0.01
M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams
deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and
110 g of deionized water were added, respectively. The flask is refluxed and/or heated for 1
to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of
15 acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,
Minneapolis, MN) are added.

In three additional solutions, 0.25 g of TMAH was added. In each solution, the
TMAH was added before, during and after the refluxing step, respectively.

20

Synthesis of absorbing material containing 9-anthracene carboxy-methyl trimethoxysilane and a pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59
25 grams MTMOS, 60 grams 9-anthracene carboxy-methyl trimethoxysilane, 0.6 grams 1.0 M,
10 M and pure lactic acid (added to three separate solutions, respectively) and 72 grams
deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and
110 g of deionized water were added, respectively. The flask is refluxed and/or heated for 1
to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of

acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

In three additional solutions, 1.5 g of potassium hydroxide was added. In each solution, the potassium hydroxide was added before, during and after the refluxing step, 5 respectively.

Synthesis of absorbing material containing 9-anthracene carboxy-propyl triethoxysilane and a pH tuning agent

10 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59 grams MTMOS, 60 grams 9-anthracene carboxy-propyl triethoxysilane, 0.6 grams 0.1 M, 0.01 M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added, respectively. The flask is refluxed and/or heated for 1 15 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

In three additional solutions, 0.5 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

20

Synthesis of absorbing material containing 9-anthracene carboxy-methyl tripropoxysilane and a pH tuning agent

25 In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59 grams MTMOS, 60 grams 9-anthracene carboxy-methyl tripropoxysilane, 0.6 grams 1.0 M, 10 M and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask is refluxed and/or heated for 1 to 12 hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of

acetone, 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M, Minneapolis, MN) are added.

In three additional solutions, 0.75 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

5

Synthesis of absorbing material containing 9-anthracene carboxy-ethyl tributoxysilane and a pH tuning agent

In a 1-liter flask 297 grams 2-propanol, 148 grams acetone, 90 grams TMOS, 59
10 grams MTMOS, 60 grams 9-anthracene carboxy-ethyl tributoxysilane, 0.6 grams 1.0 M, 10 M
and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized
water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of
deionized water were added, respectively. The flask is refluxed and/or heated for 1 to 12
hours. To the solution, 115 grams of butanol, 488 grams 2-propanol, 245 grams of acetone,
15 329 grams of ethanol, 53 grams deionized water and 3.8 grams of 10% FC 430 (3M,
Minneapolis, MN) are added.

In three additional solutions, 1.00 g of TMAH was added. In each solution, the
TMAH was added before, during and after the refluxing step, respectively.

20

EXAMPLE 19

**Synthesis of absorbing material containing phenyltriethoxysilane
and a pH tuning agent**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles)
acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6
grams 1.0 M, 10 M and pure acetic acid (added to three separate solutions, respectively) and
72 grams deionized water were combined. In two other solutions containing 10 M acetic
acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed

and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added. Thickness=1727 Å, n= 1.957, k = 0.384.

5 In three additional solutions, 1.00 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

Synthesis of absorbing material containing phenyltrimethoxysilane and a pH tuning agent

10

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6 grams 0.1 M, 0.01 M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

15 In three additional solutions, 1.00 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

Synthesis of absorbing material containing phenyltripropoxysilane and a pH tuning agent

25

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6 grams 1.0 M, 10 M and pure lactic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or

heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

5 In three additional solutions, 0.75 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing phenyltributoxysilane
and a pH tuning agent**

10 In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 104 grams (0.432 moles) phenyltriethoxysilane, 0.6 grams 1.0 M, 10 M and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed 15 and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of Butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added.

In three additional solutions, 0.50 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

EXAMPLE 20

**Synthesis of absorbing material containing
4-ethoxyphenylazobenzene-4-carboxy-methyl
5 triethoxysilane and a pH tuning agent**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 1.0 M, 10 M 10 and pure acetic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M acetic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams 15 (0.528 moles) deionized water were added.

In three additional solutions, 0.50 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

**Synthesis of absorbing material containing
20 4-ethoxyphenylazobenzene-4-carboxy-ethyl triethoxysilane**

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 1.0 M, 10 M 25 and pure lactic acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 10 M lactic acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams 30 (0.528 moles) deionized water were added.

In three additional solutions, 0.25 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

5 **Synthesis of absorbing material containing**

4-methoxyphenylazobenzene-4-carboxy-propyl triethoxysilane

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 0.1 M, 0.01 10 M and 1.0 M nitric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M nitric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422 moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams 15 (0.528 moles) deionized water were added.

In three additional solutions, 0.10 g of APTEOS was added. In each solution, the APTEOS was added before, during and after the refluxing step, respectively.

20 **Synthesis of absorbing material containing**

4-methoxyphenylazobenzene-4-carboxy-propyl trimethoxysilane

In a 1-liter flask 297 grams (4.798 moles) 2-propanol, 148 grams (2.558 moles) acetone, 123 grams (0.593 moles) TEOS, 77 grams (0.432 moles) MTEOS, 44.5 grams (0.13 moles) 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 0.6 grams 0.1 M, 0.01 25 M and 1.0 M hydrochloric acid (added to three separate solutions, respectively) and 72 grams deionized water were combined. In two other solutions containing 0.1 M hydrochloric acid, 90 g and 110 g of deionized water were added, respectively. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 57 grams (0.769 moles) of butanol, 88 grams (1.422

moles) 2-propanol, 44 grams (0.758 moles) of acetone, 59 grams (1.227 moles) of ethanol, 9.5 grams (0.528 moles) deionized water were added. $n = 1.499$, $k = 0.162$ at 365 nm.

In three additional solutions, 0.50 g of TMAH was added. In each solution, the TMAH was added before, during and after the refluxing step, respectively.

5

EXAMPLE 21

Synthesis of an absorbing material containing

PGMEA and a pH tuning agent

10

In a 1-liter flask, 504.829 g of PGMEA, 123.6 grams TEOS, 76.9 grams MTEOS, 5.608 grams 0.1 M nitric acid and 66.869 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 43.777 grams of butanol was added. The solution was filtered to be used in the pH tuning experiments.

15

In another 1-liter flask, 297 grams 2-propanol, 148.560 grams acetone, 139.902 grams TEOS, 19.10 grams MTEOS, 51.7 g PTEOS, 5.624 grams 0.1 M nitric acid and 66.827 grams deionized water were combined. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, 43.93 grams of butanol was added. The solution was filtered to be used in the pH tuning experiments.

20

The two solutions prepared were combined, and a pH tuning agent, APTEOS, was added to 6 separate solutions of 650 g of the combined material that has a starting pH of about 1.7. The APTEOS was added in the following amounts and gave the following pH: a) 1.49 g (pH = 8.07); b) 0.26 g (pH = 7.12); c) 0.1 g (pH = 6.29); d) 0.06 (pH = 5.50); e) 0.03 g (pH = 2.49); f) 0 grams (pH = 1.76). The solutions were then dispensed, followed by a 3000 rpm thickness spin for 20 seconds, and baked at 80°C and at 180°C for one minute each. Optical properties were measured with an N & K Technology Model 1200 analyzer. Optical properties follow for each of the A-F solutions shown above:

a) Thickness = 1686 Angstroms; $k = 0.297$; $n = 1.802$; etch ratio(er) = 9.33

b) Thickness = 1332 Angstroms; k = 0.295; n = 1.802; etch ratio(er) = 8.5

c) Thickness = 1298 Angstroms; k = 0.294; n = 1.802; etch ratio(er) = 8.316

d) Thickness = 1292 Angstroms; k = 0.293; n = 1.802; etch ratio(er) = 8.17

e) Thickness = 1304.9 Angstroms; k = 0.292; n = 1.802; etch ratio(er) = 8.01

5 f) Thickness = 1263.9 Angstroms; k = 0.289; n = 1.802; etch ratio(er) = 7.83

EXAMPLES 22 - 45

The following runs were made according to the matrix:

Part Type	Blocks	PGMEA	EtOH	TEOS	MTEOS	PTEOS
0	1	0.5	0.5	1	1	1
1	1	0.2	0.8	1	1	1
1	1	0.8	0.2	1	1	1
0	1	0.5	0.5	-1	1	1
1	1	0.2	0.8	-1	1	1
1	1	0.8	0.2	-1	1	1
0	1	0.5	0.5	1	-1	1
1	1	0.2	0.8	1	-1	1
1	1	0.8	0.2	1	-1	1
0	1	0.5	0.5	-1	-1	1
1	1	0.2	0.8	-1	-1	1
1	1	0.8	0.2	-1	-1	1
0	1	0.5	0.5	1	1	-1
1	1	0.2	0.8	1	1	-1
1	1	0.8	0.2	1	1	-1
0	1	0.5	0.5	-1	1	-1
1	1	0.2	0.8	-1	1	-1
1	1	0.8	0.2	-1	1	-1
0	1	0.5	0.5	1	-1	-1
1	1	0.2	0.8	1	-1	-1
1	1	0.8	0.2	1	-1	-1
0	1	0.5	0.5	-1	-1	-1
1	1	0.2	0.8	-1	-1	-1
1	1	0.8	0.2	-1	-1	-1

10 In a 1-liter flask, [356 to 89] grams of PGMEA, [356 to 89] grams of EtOH, 5.608 grams 0.1 M nitric acid and 66.869 grams deionized water were combined. [140 to 0] grams TEOS, [19 to 0] grams MTEOS and [52 to 0] grams PTEOS were then added. The flask was refluxed and/or heated for 1 to 12 hours. To the solution, [140 to 0] grams TEOS, [52 to 0] grams MTEOS and [52 to 0] grams PTEOS were added. The flask was refluxed and / or heated for 1 to 12 hours. The solutions were diluted to a desired thickness then analyzed.

15

Run #	Mn	Mw	Mp	Mz	Mz+1	Polydispersity	T avg	Film Quality	Mass Lost	10% delta Th	5% Delta Th	-2.3% Delta Th	Ne 89 lost
1	711	997	754	1336	1674	1.40266	3855	2	9.65	-34	-50	-53	307
2	649	887	734	1177	1482	1.36826	4121	3	9.47	-39	-65	-59	360
3	770	1204	401	1738	2259	1.56311	3544	1	8.12	-48	-47	-43	191
4	651	1134	407	1818	2434	1.74309	3592	2	9.24	-6	-26	-24	379
5	635	1011	404	1513	1990	1.59247	3688	3	7.23	-22	-50	-51	462
6	804	1144	768	1553	1955	1.42382	3752	2	9.41	1	-1	-1	277
7	760	1062	772	1428	1801	1.39791	3781	1	NA	-48	-53	-52	349
8	686	923	755	1206	1497	1.34554	3971	3	9.86	-55	-52	-54	465
9	788	1242	408	1797	2326	1.57505	3406	1	9.67	-20	-35	-34	226
10	655	1038	409	1525	1979	1.58485	3556	2	8.15	-31	-46	-41	358
11	621	981	410	1394	1813	1.54735	3813	3	10.40	-45	-59	-61	432
12	680	916	568	1231	1573	1.34787	3743	3	7.96	-13	-20	-15	252
13	688	954	408	1307	1681	1.388	3834	2	10.04	-23	-50	-40	352
14	666	1427	413	2731	3949	2.14366	3115	2	8.07	-29	-57	-36	467
15	741	1141	414	1715	2294	1.5397	3365	1	8.03	-10	-24	-24	262
16	668	1358	414	2448	3492	2.03209	3204	1	6.84	-42	-50	-51	345
17	750	1036	764	1379	1727	1.38086	4060	3	10.55	-41	-39	-70	456
18	869	1420	413	2125	2817	1.63471	3370	1	8.93	-33	-36	-33	225
19	719	1016	565	1427	1868	1.41367	3642	2	10.73	-16	-38	-30	441
20	672	908	410	1224	1568	1.35097	3829	3	6.79	-30	-57	-50	504
21	772	1172	413	1732	2281	1.51832	3246	1	8.93	-4	-14	-9	310
22	779	1099	766	1482	1871	1.41068	3864	2	9.89	-32	-56	-59	348
23	711	986	743	1278	1605	1.35985	4152	3	13.32	-44	-67	-53	493
24	795	1263	749	1845	2427	1.58804	3479	1	9.35	-39	-50	-38	194

EXAMPLE 46

Via first copper dual damascene patterning through ultra low k dielectrics (dielectric constant less than about 3) is very difficult. The main problem is the selective removal of the 5 sacrificial fill material from these ultra-low k dielectric materials. Previous work has shown that Si-O fill material (either UV, absorbing or transparent fill material) is the optimum material platform if the dielectric layer is Si-O based. To improve the removal selectivity, the fill material is made chemically weaker through the addition of a material modification agent, such as those described herein. However, the Si-O fill material needs to be balanced so that 10 both resistance to 2.5% TMAH based photoresist developer, resistance to the solvents comprising the photoresist or if the Si-O fill material is transparent, the absorbing composition, and at the same time showing a highly selective strip to the ultra-low k dielectric materials, coatings and/or films.

To solve this problem the photoresist can be patterned directly on the Si-O material. In 15 order to be patternable, the fill material should be resistant to 2.5% photoresist developer and to the solvents that comprise ArF, KrF and other type of photoresists. An absorbing composition layer must then be applied on top of the chemically weak Si-O based fill material. Surprisingly, resistance can be maintained to non-aqueous solvents (in this case PGMEA) while at the same time allowing for complete removal by a standard photoresist 20 developer (2.5% TMAH in water) system. Such a contrast in chemical resistance means that an organic absorbing composition layer should be coated onto an extremely weak Si-O film. Photoresist patterning would then occur on the organic absorbing composition layer and not

on the Si-O layer. Since the Si-O can be rapidly removed in mild 2.5% TMAH solutions, it can also be rapidly removed in other fluoride and more aggressive alkaline chemistries. Such an increase in strip rate provides the selectivity to ultra low k films that is needed.

To a Si-O based organo-siloxane solution (in this case we used a 248 nm absorbing composition), we add polyethylene oxide porogen (in the study conducted 2.2% of polyethylene oxide was used). The films are cast onto wafers containing vias (via first copper dual damascene pattern), and then baked to a temperature between about 250 and 275°C. Our data shows that the "porous" 248 nm absorbing composition film is resistant to PGMEA at this bake temperature. It is also 75°C above the bake temperature required by the absorbing composition/anti-reflective process (anywhere between 170 and 220°C). Next an organic absorbing composition/anti-reflective film is coated and baked on top of the Si-O layer. A thinner organic absorbing composition/anti-reflective layer can be used as the via fill is handled by the weak Si-O based layer. A thinner organic absorbing composition/anti-reflective layer facilitates the pattern transfer of photoresist through and into the Si-O and ultra-low k layer. Also, since the Si-O layer is now so weak it can be coated to sufficient thickness to improve planarization. Also the Si-O layer can be made absorbing at the patterning wavelength thus no longer placing a thickness constraint on the organic absorbing composition/anti-reflective. The organic absorbing composition/anti-reflective layer can be made sufficiently thin to act simply as a cap to the weak Si-O film. Making the organic absorbing composition/anti-reflective so thin further improves the ability to accurately transfer through the use of plasma etch the imaged pattern in the resist into the dielectric below.

Photoresist is then deposited and then trench patterned onto the organic absorbing composition/anti-reflective layer. The trench pattern is then etched through the organic absorbing composition/anti-reflective layer, the Si-O layer and into the ultra-low k layer. Once the etch is complete the remaining photoresist is removed and organic absorbing composition/anti-reflective is removed, followed by the removal of the remaining Si-O layer. Now the trench-via pattern is defined and ready for metalization.

In summary, the porous film is baked to a temperature too low to drive out the porogen. The porogen conduits are left behind within the Si-O anti-reflective coating film that when exposed to 2.3% TMAH is completely removed. However when exposed to PGMEA nothing occurs.

Thus, specific embodiments and applications of compositions and methods to produce inorganic-based materials, spin-on materials, spin-on inorganic materials and spin-on glass materials comprising absorbing compounds and that comprise at least one material modification agent, such as the at least one porogen, the at least one high-boiling solvent, the 5 at least one leveling agent, the at least one densifying agent, the at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein.

10 The inventive subject matter, therefore, is not to be restricted except in the spirit of the appended claims. Moreover, in interpreting both the specification and the claims, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be interpreted as referring to elements, components, or steps in a non-exclusive manner, indicating that the referenced 15 elements, components, or steps may be present, or utilized, or combined with other elements, components, or steps that are not expressly referenced.

Description	Condition	Days @ 40C GPC					Thickness (Å) at 2000RPMz					pH	
		Days	Mn	Mw	Mp	Mz	Mz+1	Polydispersity	T avg	T stdv	T min	T max	
POR pH=5	Initial	0	1324	2389	2511	3774	5234	1.804218	1936	12	1922	1958	99.3 5.39
	Sample#1	4	1652	3647	2930	6651	9946	2.207179	1945	10	1933	1962	99.4 4.60
	Sample#2	7	1757	4571	3055	9652	16567	2.601320	1974	15	1944	1997	99.5 4.41
POR pH=3	Initial	0	1041	1505	771	2086	2700	1.445452	1954	7	1945	1965	99.4 4.42
	Sample#1	4	1233	2074	1780	3360	4883	1.682888	1950	13	1935	1971	99.4 3.43
	Sample#2	7	1294	2589	2373	4776	7576	2.001626	1964	13	1947	1988	99.5 3.29
POR pH=1.5	Initial	0	985	1358	770	1802	2247	1.377910	1895	10	1874	1910	99.3 1.93
	Sample#1	4	1033	1403	1187	1827	2229	1.358056	1911.91	16	1885	1926	99.3 1.94
	Sample#2	7	1078	1547	1338	2090	2639	1.434647	1885.55	8	1874	1899	99.3 2.03
2:1 PGMEA/EtOH pH=5	Initial	0	1264	2559	2704	4288	6286	2.024211	1899	9	1889	1914	99.3 5.25
	Sample#1	4	1637	3682	2949	6595	9741	2.248779	1901	12	1886	1918	99.3 4.37
	Sample#2	7	1720	4897	3043	11500	25069	2.847876	1920	12	1905	1940	99.4 4.12
2:1 PGMEA/EtOH pH=3	Initial	0	918	1288	744	1759	2253	1.402608	1909	9	1900	1930	99.3 3.92
	Sample#1	4	1103	2014	1786	3444	5135	1.825808	1911	16	1887	1936	99.3 3.19
	Sample#2	7	1298	2931	2583	5936	10091	2.258633	1908	12	1896	1932	99.4 3.05
2:1 PGMEA/EtOH pH=1.5	Initial	0	854	1189	746	1591	1992	1.392050	1852	9	1833	1866	99.3 1.89
	Sample#1	4	1046	1450	1204	1915	2360	1.385914	1865	8	1851	1876	99.3 1.96
	Sample#2	7	1159	1744	1502	2441	3191	1.505260	1888	75	1858	2087	99.1 1.91
2:1 IPA/PGMEA pH=5	Initial	0	1189	2410	2579	3919	5539	2.027078	1960	11	1949	1979	99.4 5.31
	Sample#1	4	1475	3798	2980	7128	10726	2.575447	1974	10	1962	1992	99.5 4.09
	Sample#2	7	1599	4397	2997	9195	16139	2.749307	1972	13	1957	1998	99.5 4.02
2:1 IPA/PGMEA pH=3	Initial	0	858	1289	749	1805	2314	1.502677	1983	16	1967	2016	99.4 3.91
	Sample#1	4	1166	2402	2252	4330	6551	2.059391	1960	13	1935	1982	99.4 3.18
	Sample#2	7	1203	2694	2491	5199	8364	2.239049	1967	10	1956	1986	99.5 3.15
2:1 IPA/PGMEA pH=1.5	Initial	0	838	1220	752	1668	2099	1.456108	1895	8	1885	1909	99.3 2.03
	Sample#1	4	1065	1517	1439	2024	2493	1.425050	1914	19	1882	1937	99.3 2.12
	Sample#2	7	1101	1637	1507	2263	2912	1.486570	1855	16	1833	1873	99.3 2.12
2:1 EtOH/PGMEA pH=5	Initial	0	1101	2488	2700	4182	5873	2.258769	2046	9	2036	2063	99.5 5.55
	Sample#1	4	1340	3517	2930	6569	9938	2.625218	2025	16	2003	2058	99.5 4.50
	Sample#2	7	1441	4167	3030	8511	14250	2.892158	2053	15	2032	2079	99.5 4.36
2:1 EtOH/PGMEA pH=3	Initial	0	698	1007	722	1407	1835	1.443613	2076	15	2060	2110	99.5 3.76
	Sample#1	4	937	1799	382	3263	5097	1.919020	2048	16	2022	2075	99.5 3.17
	Sample#2	7	1035	2219	383	4307	7001	2.143891	2052	14	2034	2081	99.5 3.19
2:1 EtOH/PGMEA pH=1.5	Initial	0	694	940	727	1238	1548	1.353852	1914	7	1905	1926	99.2 2.10
	Sample#1	4	986	1322	762	1717	2108	1.340978	1971	19	1935	2000	99.3 2.13
	Sample#2	7	1068	1490	1200	1989	2509	1.395892	2039	21	2007	2066	99.5 2.10

Table 1

Refiner Time (hrs)	Temp (C)	GPC	Low MW Species						Optical Properties						Normalized GC										
			Mn	Mw	M _p	M _z	M _{z+1}	Polydispersity	% Area	% Height	T _{avg}	T _{std}	T _{min}	T _{max}	% Fit	n	k	T _{max}	R _{calc}	Water	Ethanol	Buanol	PGMEA	Density	pH
4	50	682	924	731	1213	1512	1.354	3.62	18.56	30.91	27	30.66	31.44	99.3	1.829	0.276	0.0971	0.0959	5.00	58.2	5.73	20.0	0.8900	2.33	11.04
6	60	775	1057	744	1395	1741	1.364	2.06	11.69	30.79	18	30.52	31.03	99.3	1.827	0.287	0.0974	0.0960	4.96	57.9	5.85	20.3	0.8897	2.34	10.99
8	70	879	1225	757	1634	2047	1.393	1.05	7.2	30.75	30	30.33	31.28	99.33	1.831	0.277	0.0972	0.0961	4.90	57.5	6.04	20.5	0.8894	2.37	11.01
6	60	783	1076	749	1428	1791	1.373	1.71	10.96	30.63	22	30.40	31.06	99.32	1.827	0.281	0.0954	0.0957	4.91	57.9	5.91	20.5	0.8896	2.35	10.79
8	50	727	1001	743	1332	1678	1.376	2.53	14.02	30.83	20	30.54	31.15	99.33	1.825	0.284	0.0968	0.0955	4.90	57.7	5.88	20.6	0.8998	2.41	10.91
4	70	792	1099	750	1472	1859	1.388	2.12	12.32	30.76	20	30.44	31.06	99.33	1.825	0.284	0.0967	0.0956	4.85	57.6	5.93	20.7	0.8997	2.37	10.91

Table 2

Heat Ramp (1L Flask Temperature, °C)

Run#	1	2	3	4	5	6
Run 1D	4hr / 50C	6hr / 60C	8hr / 70C	6hr / 60C	8hr / 50C	4hr / 70C
Manle 1D	6	7	5	6	7	5
Target (°C)	50	60	70	60	50	70
Pre-wafer temperature	16.2	16.5	14.6	16.2	16.8	14.4
Time (min)						
0	18.6	19.0	17.0	19.6	20.0	17.9
5	22	22.8	20	23.2	24	21
10	29	29.8	24.9	30	31	25.9
15	38	38.8	31.5	39.1	40	32.8
20	46.5	47.4	38	48.2	48.1	39.7
25	52.9	55.7	44.6	56.3	53.8	46
30	55.6	60.5	49.8	61.4	56.4	51.8
35	55.7	62.3	53.9	63.5	56.2	56.5
40	54.1	62.6	56.9	63.9	55	60.1
45	52	62	59	62.7	53.4	63
50	49.6	60.7	61	61.4	51.7	65.3
55	48	59.9	62.5	59.9	49.6	67
60	46.6	58.8	63.6	58.8	48	68.1
Buanol Temp (°C)						
240	50					68
360		60		59.9		
480			67.2		49.4	

Table 3

Table 4 Part 1

MATERIAL INFORMATION						VIA FILL (est.error: ±10%)		VOIDING	
Sample Description	Target Thickness	Thickness (Å)	Spin (rpm)	Mw on Spin date	Days Aged	Viafill (µm)	% Via fill	Yes	No
Uncoated Wafer									
POR pH = 1.5	2000 Å	1945	1500	1286	4 days @ -20C	0.91	114%		X
						0.53	46%		X
						0.83	70%		X
						0.89	76%		X
						0.60	54%		X
						0.69	66%		X
						0.80	76%		X
						0.61	67%		X
	2500 Å	2562	1580	1303	0	1.14	108%		X
						0.43	38%		X
						0.77	65%		X
						0.79	67%		X
						0.80	72%		X
						1.01	97%		X
						1.10	107%		X
						0.97	106%		X
	3500 Å	3499	1500	1305	0	0.90	105%		X
						1.13	99%		X
						1.20	101%		X
						1.24	106%		X
						1.00	90%		X
						1.14	110%		X
						1.17	114%		X
						1.06	116%		X
POR pH=1.5 + high bp solvent	2000 Å	2061	1580	1295	0	1.03	116%		X
						0.44	39%		X
						0.69	63%		X
						1.04	89%		X
						0.74	67%		X
						0.83	79%		X
						1.03	100%		X
						0.80	81%		X
	2500 Å	2447	1760	1304	0	0.97	113%		X
						0.83	73%		X
						0.97	82%		X
						1.17	100%		X
						0.81	73%		X
						0.93	89%		X
						1.04	101%		X
						0.83	85%		X
	3500 Å	3480	1660	1304	0	1.17	137%		X
						1.17	103%		X
						1.21	102%		X
						1.31	112%		X
						1.11	100%		X
						1.14	110%		X
						1.23	119%		X
						1.03	106%		X

Table 4 Part 1 (cont'd)

VIA TEST STRUCTURE INFORMATION						
Target Thickness	Sem Location	Via Diameter (μm)	Pitch (μm)	Via Depth (μm)	Pitch : Diameter	Depth : Diameter
	isolated	0.14	0.90	0.86	6.3	6.0
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.91	1.9	6.4
2000 Å	isolated	0.14	0.90	0.80	6.3	5.6
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.91	1.9	6.4
2500 Å	isolated	0.14	0.90	1.06	6.3	7.4
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.91	1.9	6.4
3500 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.91	1.9	6.4
2000 Å	isolated	0.14	0.90	0.89	6.3	6.2
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.09	2.0	4.8
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.99	1.9	6.9
2500 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.97	1.9	6.8
3500 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1-1	0.23	0.39	1.14	1.7	5.0
	1-3	0.23	0.46	1.19	2.0	5.2
	1-5	0.24	0.54	1.17	2.2	4.8
	3-1	0.19	0.30	1.11	1.6	6.0
	3-3	0.19	0.34	1.04	1.8	5.6
	3-5	0.19	0.37	1.03	2.0	5.5
	6-1	0.14	0.27	0.97	1.9	6.8

Table 4 Part 2

MATERIAL INFORMATION						VIA FILL (est.error: ±10%)		VOIDING	
Sample Description	Target Thickness (Å)	Thickness (Å)	Spin (rpm)	Mw on Spin date	Days Aged	Via fill (µm)	% Via fill	Yes	No
POR (pH=5.6)	2000 Å	2001	1670	3418	4 days @ -20C	0.99	115%	X	
						0.21	19%		X
						0.26	22%	X	
						0.29	24%	X	
						0.29	26%	X	
						0.29	27%	X	
						0.29	28%	X	
						0.30	33%	X	
	2500 Å	2537	1790	3007	0	1.09	107%	X	
						0.29	25%	X	
						0.30	25%	X	
						0.30	26%	X	
						0.29	26%	X	
						0.31	30%	X	
						0.37	36%	X	
						0.33	36%	X	
	3500 Å	3506	1500	3334	0	1.14	133%	X	
						0.70	61%	X	
						0.99	83%	X	
						1.27	109%	X	
						0.59	53%	X	
						0.80	77%	X	
						0.91	89%	X	
						0.91	100%	X	
POR + high bp solvent	2000 Å	2042	1700	3399	0	0.94	103%		X
						0.23	20%		X
						0.37	31%		X
						0.43	37%		X
						0.26	23%		X
						0.36	34%		X
						0.43	42%		X
						0.37	41%		X
	2500 Å	2509	1940	3101	0	1.10	128%		X
						0.40	35%		X
						0.50	42%		X
						0.57	49%		X
						0.40	36%		X
						0.43	41%		X
						0.57	56%		X
						0.46	50%		X
	3500 Å	3511	1590	3414	0	1.19	138%		X
						0.79	69%		X
						1.09	92%	X	
						1.24	105%	X	
						0.71	64%		X
						0.86	82%		X
						1.00	97%	X	
						0.99	108%	X	

Table 4 Part 2 (cont'd)

VIA TEST STRUCTURE INFORMATION						
Target Thickness	Sem Location	Via Diameter (μm)	Pitch (μm)	Via depth (μm)	Pitch : Diameter	Aspect Ratio (Depth:Dia.)
2000 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4
2500 Å	isolated	0.14	0.90	1.01	6.3	7.1
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.18	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4
3500 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4
2000 Å	isolated	0.14	0.90	0.91	6.3	6.4
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4
2500 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4
3500 Å	isolated	0.14	0.90	0.86	6.3	6.0
	1 - 1	0.23	0.39	1.14	1.7	5.0
	1 - 3	0.23	0.46	1.19	2.0	5.2
	1 - 5	0.24	0.54	1.17	2.2	4.8
	3 - 1	0.19	0.30	1.11	1.6	6.0
	3 - 3	0.19	0.34	1.04	1.8	5.6
	3 - 5	0.19	0.37	1.03	2.0	5.5
	6 - 1	0.14	0.27	0.91	1.9	6.4

PARENT QC RESULTS

x = 66.85 g

Spin Conditions: 1500 rpm (20s)
Bake Conditions: 150/250 C. n2 (50s)

Water Content GPC

Water Content	Mn	Mw	Mp	Mz	Mz+1	Polydispersity	T _{avg}	T _{sidew}	T _{min}	T _{max}	% Fit	pH	Density	GC (Normalized)	Solids					
1.0x	762	1131	725	1576	2011	1.483833	3725.78*	21.324	3694.2	3758.9	99.33	2.276	0.8542	5.5746	24.6763	41.3693	22.0987	6.2811	100	11.01
0.9x	696	1017	739	1409	1795	1.461169	5511.55	57.127	5438	5607.1	98.54	1.998	0.8525	4.6764	25.2699	41.8127	22.0606	6.1604	100	11.47
0.8x	644	925	399	1276	1637	1.435518	5397.48	46.694	5308.4	5458.2	99.09	1.836	0.8504	3.8861	23.6460	43.4587	22.8314	6.1779	100	11.72

Table 5

CHILD QC RESULTS

Spin Conditions: 1500 rpm (20s)
Bake Conditions: 150/250 C. n2 (50s)

Sample	Parent Water Content	Base	Dilution Factor	Time of Dilution	GPC Prep and Spin	Time Lag	Gpc	Thickness (Å) on 4" Wafers	% Fit									
1	1.0x	APTEOS	0.75	12:00 PM	1:00 PM	Time	Hours	Mn	Mw	Mp	Mz	Mz+1	Polydispersity	T avg	T sidev	T min	T max	% Fit
2				4:00 PM	4	1436	2771	2613	4398	6002	1.930054	2095.32	19.181	2072.8	2133.4	99.55		
3				7:30 PM	7.5	1467	2988	2923	4834	6621	2.037003	2094.67	30.493	2050.8	2144.8	99.44		
4				1:30 PM	25.5	1758	3672	2970	6178	8876	2.088918	2098.45	18.325	2075.1	2128.7	99.51		
1	0.9x	APTEOS	0.86	12:30 PM	1:00 PM	1	930	1805	396	2749	3536	1.940289	2011.78	22.797	1987.1	2050.4	99.45	
2				4:00 PM	4	1095	2421	2717	3847	5088	2.211078	1977.24	17.486	1959.8	2014.8	99.40		
3				7:30 PM	7.5	1162	2670	2817	4320	5797	2.298419	1976.41	17.612	1953.2	2009.7	99.41		
4				1:30 PM	25.5	1218	3079	2803	5250	7345	2.528687	1964.98	20.458	1936.8	2006.5	99.34		
1	0.8x	APTEOS	0.86	12:00 PM	1:00 PM	1	857	1610	397	2441	3122	1.880068	2046.81	25.542	2020.8	2106.4	99.42	
2				4:00 PM	4	1009	2172	2555	3429	4502	2.153646	2038.46	13.784	2022.9	2067	99.47		
3				7:30 PM	7.5	1336	2529	2682	3813	4965	1.892464	2013.19	29.402	1971.9	2071	99.32		
4				:30 PM	25.5	1193	2829	2810	4628	6264	2.37155	2014.58	26.576	1868.8	2058.5	99.36		

A. material	film thickness (SEM - no via) (Å)	3100	thickness difference (isolated - dense) (Å)
no acetone 248 nm	film thickness between vias (Å)	3100	1285
via spacing (nm)	1815	1100	1100
120	2000	550	550
160	2550		
300			
B. material	film thickness (SEM - no via) (Å)	3050	thickness difference (isolated - dense) (Å)
1:1 High/Low MW	film thickness between vias (Å)	3050	1550
via spacing (nm)	1500	1250	1250
120	1800	700	700
160	2350		
300			
C. material	film thickness (SEM - no via) (Å)	3200	thickness difference (isolated - dense) (Å)
no acetone 248 nm w/ 0.05% BYK381	film thickness between vias (Å)	3200	1250
via spacing (nm)	1950	650	650
120	2550		
160			
300			
D. material	film thickness (SEM - no via) (Å)	3100	thickness difference (isolated - dense) (Å)
no acetone 248 nm w/ 0.4% BYK381	film thickness between vias (Å)	3100	900
via spacing (nm)	2200	700	700
120	2400	300	300
160	2800		
300			
E. material	film thickness (SEM - no via) (Å)	3200	thickness difference (isolated - dense) (Å)
no acetone 248 nm w/ 0.4% BYK380	film thickness between vias (Å)	3200	1400
via spacing (nm)	1800	1200	1200
120	2000	600	600
160	2600		
300			
F. material	film thickness (SEM - no via) (Å)	3850	thickness difference (isolated - dense) (Å)
193 nm made with DMTEOS	film thickness between vias (Å)	3850	1730
via spacing (nm)	2120	1250	1250
120	2600	850	850
160	3000		
300			
G. material	film thickness (SEM - no via) (Å)	3150	thickness difference (isolated - dense) (Å)
248 nm w/ 2% CRJ-406	film thickness between vias (Å)	3150	1450
via spacing (nm)	1700	1550	1550
120	1600	590	590
160	2560		
300			
H. material	film thickness (SEM - no via) (Å)	3200	thickness difference (isolated - dense) (Å)
no acetone 248 nm w/ 0.2% BYK381	film thickness between vias (Å)	3200	1300
via spacing (nm)	1900	1300	1300
120	1900	550	550
160	2650		
300			
I. material	film thickness (SEM - no via) (Å)	3300	thickness difference (isolated - dense) (Å)
no acetone 248 nm w/ 0.6% BYK381	film thickness between vias (Å)	3300	1400
via spacing (nm)	1900	1400	1400
120	1900	300	300
160	3000		
300			
J.	material		
no acetone 248 nm w/ 0.8% BYK380	film thickness (SEM - no via) (Å)	3100	thickness difference (isolated - dense) (Å)
via spacing (nm)	film thickness between vias (Å)	3100	1300
120	1800		
160	2400	700	700
300			
K. material	film thickness (SEM - no via) (Å)	3600	thickness difference (isolated - dense) (Å)
193 nm made with DMTEOS	film thickness between vias (Å)	3600	1600
via spacing (nm)	2000	750	750
120	2850		
160			
300			
L. material	film thickness (SEM - no via) (Å)	3000	thickness difference (isolated - dense) (Å)
no acetone 248 nm w/ 1.5% BYK380	film thickness between vias (Å)	3000	1600
via spacing (nm)	1400	1400	1400
120	1600	800	800
160	2200		
300			
M. material	film thickness (SEM - no via) (Å)	3200	thickness difference (isolated - dense) (Å)
no acet. 248 nm (1:1 Hi/Lo MW) w/ 0.3% BYK381	film thickness between vias (Å)	3200	1230
via spacing (nm)	1970	1200	1200
120	2000	800	800
160	2400		
300			

Table 7

CLAIMS

We claim:

1. An absorbing composition comprising at least one inorganic-based compound, at least one incorporatable absorbing compound, and at least one material modification agent.
- 5 2. The absorbing composition of claim 1, wherein the at least one material modification agent comprises the at least one porogen, the at least one high-boiling solvent, the at least one leveling agent, the at least one densifying agent, the at least one capping agent, the at least one catalyst, the at least one replacement solvent, at least one adhesion promoting material, at least one pH tuning agent, and/or a combination thereof.
- 10 3. The composition of claim 2, wherein the incorporatable absorbing compound is an organic-based compound.
4. The composition of claim 2, wherein the absorbing compound strongly absorbs light over at least an approximately 0.5 nm wide wavelength range at wavelengths less than 375 nm.
- 15 5. The composition of claim 2, wherein the absorbing compound strongly absorbs light over at least an approximately 10 nm wide wavelength range at wavelengths less than 375 nm.
6. The composition of claim 4, wherein the range comprises wavelengths less than about 260 nm.
- 20 7. The composition of claim 2, wherein the absorbing compound comprises at least one benzene ring and a reactive group selected from the group comprising hydroxyl groups, amine groups, carboxylic acid groups and substituted silyl groups.
8. The composition of claim 7, wherein the absorbing compound comprises two or more benzene rings.
- 25 9. The composition of claim 8, wherein the two or more benzene rings are fused.
10. The composition of claim 7, wherein the organic absorbing compound comprises an absorbing compound comprising anthraflavic acid, 9-anthracene carboxylic acid,

9-anthracene methanol, alizarin, quinizarin, primuline,
2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid,
triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-alkyl triethoxysilane,
phenyltriethoxysilane, 10-phenanthrene carboxy-methyl triethoxysilane, 4-
5 phenylazophenol, 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 4-
methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane or mixtures thereof.

11. The composition of claim 2, wherein the inorganic-based compound comprises a
silicon-based compound.

12. The composition of claim 11, wherein the silicon-based compound comprises a
10 polymer.

13. The composition of claim 12, wherein the polymer comprises an organosiloxane
compound, such as methylsiloxane, methylsilsesquioxane, phenylsiloxane,
phenylsilsesquioxane, acrylic siloxane polymers, methylphenylsiloxane,
methylphenylsilsesquioxane, silicate polymers, silazane polymers or mixtures thereof.

14. The composition of claim 12, wherein the polymer comprises hydrogensiloxane,
hydrogensilsesquioxane, organohydridosiloxane, silsesquioxane-based compounds,
derivatives of silic acid and organohydridosilsesquioxane polymers; copolymers of
hydrogensilsesquioxane and an alkoxyhydridosiloxane, hydroxyhydridosiloxane,
derivatives of silic acid or mixtures thereof.

15. The composition of claim 12, wherein the polymer is of a general formula comprising
(H_{0-1.0}SiO_{1.5-2.0})_x, where x is greater than about 4, and
(H_{0-1.0}SiO_{1.5-2.0})_n(R_{0-1.0}SiO_{1.5-2.0})_m, where m is greater than 0, the sum of n and m is
20 from about 4 to about 5000 and R is a C₁-C₂₀ alkyl group or a C₆-C₁₂ aryl group.

16. The composition of claim 2, wherein the at least one pH tuning agent comprises
25 water.

17. The composition of claim 2, wherein the at least one pH tuning agent comprises a
base.

18. The composition of claim 17, wherein the at least one base comprises an amine.

19. The composition of claim 18, wherein the amine comprises an amine-based oligomer.

20. The composition of claim 2, wherein the at least one pH tuning agent comprises an acid.
21. The composition of claim 2, wherein the at least one high-boiling solvent comprises glycerol.
- 5 22. The composition of claim 2, wherein the at least one high boiling solvent comprises carbitol.
23. The composition of claim 2, wherein the at least one high boiling solvent comprises dipropylene glycol (DPG).
24. The composition of claim 2, wherein the at least one replacement solvent comprises isopropylalcohol, ethanol, PGMEA or 2-heptanone.
- 10 25. The composition of claim 2, wherein the at least one catalyst comprises a weak acid.
26. The composition of claim 2, wherein the at least one adhesion promoter comprises a resin-based material.
27. The composition of claim 26, wherein the resin-based material comprises at least one of a phenolic-containing resin, a novolac resin, an organic acrylate resin or a styrene resin.
- 15 28. The composition of claim 2, wherein the adhesion promoter comprises a polydimethylsiloxane-based material, an ethoxy or hydroxy-containing silane monomer, a vinyl-containing silane monomer, an acrylated silane monomer or a silyl hydride compound.
- 20 29. The composition of claim 2, wherein the at least one capping agent comprises a terminating monomer.
30. The composition of claim 29, wherein the terminating monomer comprises a silane compound.
- 25 31. The composition of claim 2, wherein the at least one porogen comprises an organic compound.
32. The composition of claim 31, wherein the organic compound comprises a polymer.

33. The composition of claim 32, wherein the polymer comprises poly(ethylene oxide).
34. The composition of claim 2, wherein the at least one porogen further comprises a catalyst.
35. The composition of claim 34, wherein the catalyst comprises TMAA.
- 5 36. A coating solution comprising the composition of claim 2 and an additional solvent or a solvent mixture.
37. The coating solution of claim 36, wherein the solution is between about 0.5% and about 20% by weight absorbing material.
- 10 38. The composition of claim 2, wherein the at least one densifying agent comprises an amine-based compound, water; an oxide, an alkoxide, a hydrogen halide, an acid, TMAH, an acetate-based compound, a nitrate-based compound, or combinations thereof.
- 15 39. The composition of claim 38, wherein the at least one densifying agent comprises γ -aminoalkyltrialkoxysilanes, γ -aminopropyltriethoxysilanes (APTEOS), APTEOS-N, APTEOS-acetate, ammonium acetate or combinations thereof.
40. The composition of claim 38, wherein the at least one densifying agent comprises TMAH, tetra-methyl ammonium acetate (TMAA), ammonium nitrate, tetra-methyl ammonium nitrate (TMAN) or combinations thereof.
41. The composition of claim 2, wherein the at least one material modification agent comprises a leveling agent.
- 20 42. The composition of claim 41, wherein the leveling agent comprises a polyacrylate compound.
43. The composition of claim 42, wherein the polyacrylate compound is ionic.
44. The composition of claim 42, wherein the polyacrylate compound is non-ionic.
- 25 45. A method of making an absorbing composition comprising:

combining at least one inorganic-based compound, at least one incorporatable absorbing compound, at least one material modification agent, an acid/water mixture, and one or more solvents to form a reaction mixture; and

allowing the reaction mixture to form the absorbing composition at room temperature.

5 46. The method of claim 45, wherein the material modification agent comprises at least one porogen, at least one high-boiling solvent, at least one densifying agent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof.

10 47. A method of making an absorbing composition comprising:
combining at least one inorganic-based compound, at least one incorporatable absorbing compound, at least one material modification agent, an acid/water mixture, and one or more solvents to form a reaction mixture; and
heating the reaction mixture to form the absorbing composition.

15 48. The method of claim 41, wherein the material modification agent comprises at least one porogen, at least one high-boiling solvent, at least one densifying agent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof.

20 49. A method of making an absorbing composition comprising:
combining at least one inorganic-based compound, at least one incorporatable absorbing compound, at least one material modification agent, and one or more solvents to form a reaction mixture, wherein the at least one material modification agent comprises at least one acid and water; and
heating the reaction mixture to form a absorbing material, a coating or a film.

25 50. The method of claim 49, wherein the material modification agent comprises at least one porogen, at least one high-boiling solvent, at least one densifying agent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one

leveling agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof

51. A method of making an absorbing composition comprising:
 - 5 combining at least one inorganic-based compound, at least one incorporatable absorbing compound, at least one material modification agent, and one or more solvents to form a reaction mixture, wherein the at least one material modification agent comprises at least one acid and water; and
 - allowing the reaction mixture to form a absorbing material, a coating or a film.
52. The method of claim 51, wherein the material modification agent comprises at least 10 one porogen, at least one high-boiling solvent, at least one densifying agent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof.
53. The method of one of claims 45, 47, 49 or 51, wherein the at least one absorbing 15 compound comprises at least one benzene ring and a reactive group comprising a hydroxyl group, an amine group, a carboxylic acid group, or a substituted silyl group, and wherein a silicon atom is bonded to at least one substituent on the absorbing compound that comprises an alkoxy group, an acetoxy group or a halogen atom.
54. The method of one of claims 45, 47, 49 or 51, wherein the at least one absorbing 20 compound comprises anthraflavic acid, 9-anthracene carboxylic acid, 9-anthracene methanol, alizarin, quinizarin, primuline, 2-hydroxy-4(3-triethoxysilylpropoxy)-diphenylketone, rosolic acid, triethoxysilylpropyl-1,8-naphthalimide, 9-anthracene carboxy-alkyl triethoxysilane, phenyltriethoxysilane, 10-phenanthrene carboxy-methyl triethoxysilane, 4-25 phenylazophenol, 4-ethoxyphenylazobenzene-4-carboxy-methyl triethoxysilane, 4-methoxyphenylazobenzene-4-carboxy-methyl triethoxysilane or mixtures thereof.
55. The method of one of claims 45, 47, 49 or 51, wherein the at least one inorganic-based 30 compound comprises triethoxysilane, tetraethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, tetramethoxysilane, methyltrimethoxysilane, trimethoxysilane, dimethyldimethoxysilane, phenyltriethoxysilane,

phenyltrimethoxysilane, diphenyldiethoxysilane, diphenyldimethoxysilane,
trichlorosilane, methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane,
tetrachlorosilane, chlorotriethoxysilane, chlorotrimethoxysilane,
chloromethyltriethoxysilane, chloroethyltriethoxysilane, chlorophenyltriethoxysilane,
5 chloromethyltrimethoxysilane, chloroethyltrimethoxysilane,
chlorophenyltrimethoxysilane, tetraacetoxysilane, methyltriacetoxysilane,
phneyltriacetoxysilane, diphenyldiacetoxysilane or dimethyldiacetoxysilane.

56. The method of one of claims 46, 48, 50 or 52, wherein the at least one pH tuning
agent comprises water.

10 57. The method of one of claims 46, 48, 50 or 52, wherein the at least one pH tuning
agent comprises a base.

58. The method of claim 57, wherein the at least one base comprises an amine.

59. The method of claim 58, wherein the amine comprises an amine-based oligomer.

60. The method of one of claims 46, 48, 50 or 52, wherein the at least one pH tuning
15 agent comprises an acid.

61. The method of one of claims 46, 48, 50 or 52, wherein the at least one high-boiling
solvent comprises glycerol.

62. The method of one of claims 46, 48, 50 or 52, wherein the at least one high boiling
solvent comprises carbitol.

20 63. The method of one of claims 46, 48, 50 or 52, wherein the at least one high boiling
solvent comprises dipropylene glycol (DPG).

64. The method of one of claims 46, 48, 50 or 52, wherein the at least one replacement
solvent comprises isopropylalcohol, ethanol, PGMEA or 2-heptanone.

65. The method of one of claims 46, 48, 50 or 52, wherein the at least one catalyst
25 comprises a weak acid.

66. The method of one of claims 46, 48, 50 or 52, wherein the at least one adhesion
promoter comprises a novolac resin.

67. The method of one of claims 46, 48, 50 or 52, wherein the at least one adhesion promoter comprises a resin-based material.
68. The method of claim 67, wherein the resin-based material comprises at least one of a phenolic-containing resin, a novolac resin, an organic acrylate resin or a styrene resin.
- 5 69. The method of one of claims 46, 48, 50 or 52, wherein the adhesion promoter comprises a polydimethylsiloxane-based material, an ethoxy, methoxy, acetoxy, or hydroxy-containing silane monomer, a vinyl-containing silane monomer, an acrylated silane monomer or a silyl hydride compound.
- 10 70. The method of one of claims 46, 48, 50 or 52, wherein the at least one porogen comprises an organic compound.
71. The method of claim 70, wherein the organic compound comprises a polymer.
72. The method of claim 71, wherein the polymer comprises poly(ethylene oxide).
73. The method of one of claims 46, 48, 50 or 52, wherein the at least one porogen further comprises a catalyst.
- 15 74. The method of claim 73, wherein the catalyst comprises TMAA.
75. The method of one of claims 46, 48, 50 or 52, wherein the at least one densifying agent comprises an amine-based compound, water, an oxide, an alkoxide, a hydrogen halide, an acid, TMAH, an acetate-based compound, a nitrate-based compound, or combinations thereof.
- 20 76. The method of claim 75, wherein the at least one densifying agent comprises γ -aminoalkyltrialkoxysilanes, ammonium acetate, γ -aminopropyltriethoxysilanes (APTEOS), APTEOS-N, APTEOS-acetate or combinations thereof.
77. The method of claim 75, wherein the at least one densifying agent comprises TMAH, tetra-methyl ammonium acetate (TMAA), ammonium nitrate, tetra-methyl ammonium nitrate (TMAN) or combinations thereof.
- 25 78. The method of one of claims 46, 48, 50 or 52, wherein the at least one material modification agent comprises a leveling agent.

79. The method of claim 78, wherein the leveling agent comprises a polyacrylate compound.
80. The method of claim 78, wherein the polyacrylate compound is ionic.
81. The method of claim 78, wherein the polyacrylate compound is non-ionic.
- 5 82. A method of making a coating solution containing an absorbing material comprising:
combining at least one alkoxysilane or halosilane or acetoxy silane, at least one incorporatable absorbing compound, at least one densifying agent, at least one porogen, at least one high boiling solvent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof; an acid and water mixture; and one or more solvents to form a reaction mixture; and
allowing the mixture to react at about room temperature in an exothermic fashion to form a coating solution.
- 10 83. A method of making a coating solution containing an absorbing material comprising:
combining at least one alkoxysilane, halosilane or acetoxy silane at least one incorporatable absorbing compounds; at least one porogen, at least one densifying agent, at least one high-boiling solvent, at least one catalyst, at least one replacement solvent, at least one capping agent, at least one leveling agent, at least one adhesion promoter, at least one pH tuning agent or a combination thereof; an acid/water mixture; and one or more solvents to form a reaction mixture; and
heating the reaction mixture to form a coating solution.
- 15 84. The method of either claim 82 or 83, wherein the at least one pH tuning agent comprises water.
85. The method of either claim 82 or 83, wherein the at least one pH tuning agent comprises a base.
- 20 86. The method of claim 85, wherein the at least one base comprises an amine.
87. The method of claim 86, wherein the amine comprises an amine-based oligomer.

88. The method of either claim 82 or 83, wherein the at least one pH tuning agent comprises an acid.
89. The method of either claim 82 or 83, wherein the at least one high-boiling solvent comprises glycerol.
- 5 90. The method of either claim 82 or 83, wherein the at least one high boiling solvent comprises carbitol.
91. The method of either claim 82 or 83, wherein the at least one high boiling solvent comprises dipropylene glycol (DPG).
92. The method of either claim 82 or 83, wherein the at least one replacement solvent
- 10 comprises isopropylalcohol, ethanol, PGMEA or 2-heptanone.
93. The method of either claim 82 or 83, wherein the at least one catalyst comprises a weak acid.
94. The method of either claim 82 or 83, wherein the at least one adhesion promoter comprises a resin-based material.
- 15 95. The method of claim 94, wherein the resin-based material comprises at least one of a phenolic-containing resin, a novolac resin, an organic acrylate resin or a styrene resin.
96. The method of either claim 82 or 83, wherein the adhesion promoter comprises a polydimethylsiloxane-based material, an ethoxy or hydroxy-containing silane monomer, a vinyl-containing silane monomer, an acrylated silane monomer or a silyl
- 20 hydride compound.
97. The method of either claim 82 or 83, wherein the at least one capping agent comprises a terminating monomer.
98. The method of claim 97, wherein the terminating monomer comprises a silane compound.
- 25 99. The method of either claim 82 or 83, wherein the at least one porogen comprises an organic compound.
100. The method of claim 99, wherein the organic compound comprises a polymer.

101. The method of claim 100, wherein the polymer comprises poly(ethylene oxide).
102. The method of either claim 82 or 83, wherein the at least one porogen further comprises a catalyst.
103. The method of claim 102, wherein the catalyst comprises TMAA.
- 5 104. The method of either claim 82 or 83, further comprising adding one or more dilutant solvents to the absorbing composition to produce a coating solution.
105. The method of one of claims 82 or 83, wherein the at least one densifying agent comprises an amine-based compound, water, an oxide, an alkoxide, a hydrogen halide, an acid, TMAH, an acetate-based compound, a nitrate-based compound, or combinations thereof.
106. The method of claim 105, wherein the at least one densifying agent comprises γ -aminoalkyltrialkoxysilanes, ammonium acetate, γ -aminopropyltriethoxysilanes (APTEOS), APTEOS-N, APTEOS-acetate or combinations thereof.
107. The method of claim 105, wherein the at least one densifying agent comprises TMAH, tetra-methyl ammonium acetate (TMAA), ammonium nitrate, tetra-methyl ammonium nitrate (TMAN) or combinations thereof.
- 15 108. The method of one of claims 82 or 83, wherein the at least one material modification agent comprises a leveling agent.
109. The method of claim 108, wherein the leveling agent comprises a polyacrylate compound.
- 20 110. The method of claim 108, wherein the polyacrylate compound is ionic.
111. The method of claim 108, wherein the polyacrylate compound is non-ionic.
112. A layered material comprising the absorbing composition of claim 2 coupled to a resist material.
- 25 113. A semiconductor component comprising the absorbing composition of claim 2.
114. A film comprising the absorbing composition of claim 2.
115. An electronic component comprising the absorbing composition of claim 2.

116. The composition of claim 2, wherein the absorbing composition is designed to be at least partially removed.
117. The composition of claim 112, wherein the resist material absorbs light over a wavelength range that comprises 157 nm, 193 nm, 248 nm and 365 nm.
- 5 118. The absorbing composition of claim 2, wherein the at least one porogen comprises polyethylene oxide, poly(propylene glycol) dipropylene glycol.
119. The absorbing composition of claim 2, wherein the at least one porogen comprises a molecular weight and wherein the inorganic-based compound forms a matrix.
- 10 120. The absorbing composition of claim 119, wherein the molecular weight is compatible with the solubility of the matrix.

FIG. 1A

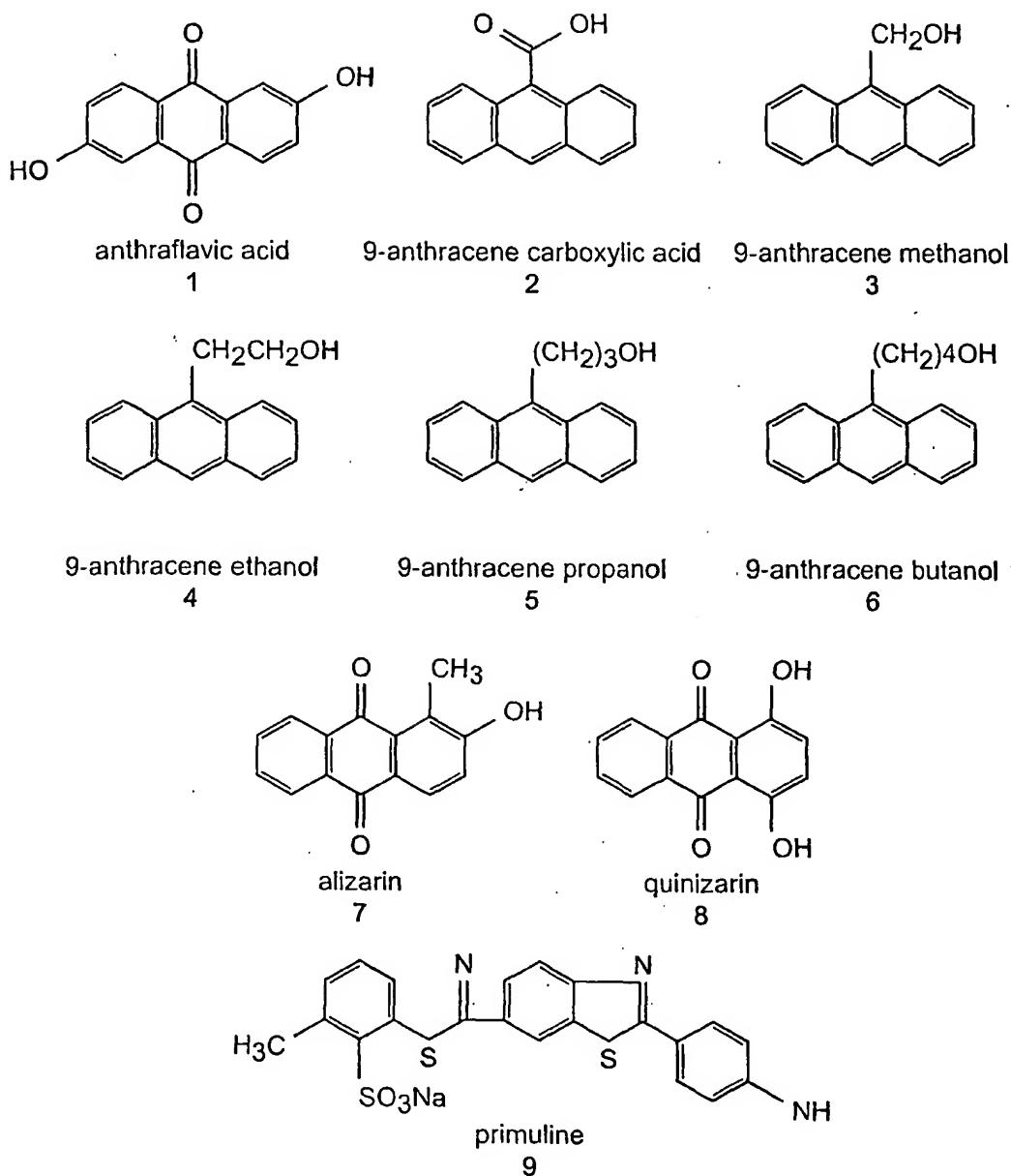
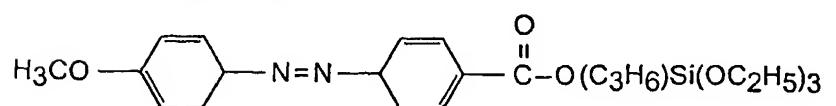


FIG. 1F



4-methoxyphenylazobenzene-4-carboxy
propyl triethoxysilane

FIG. 1B

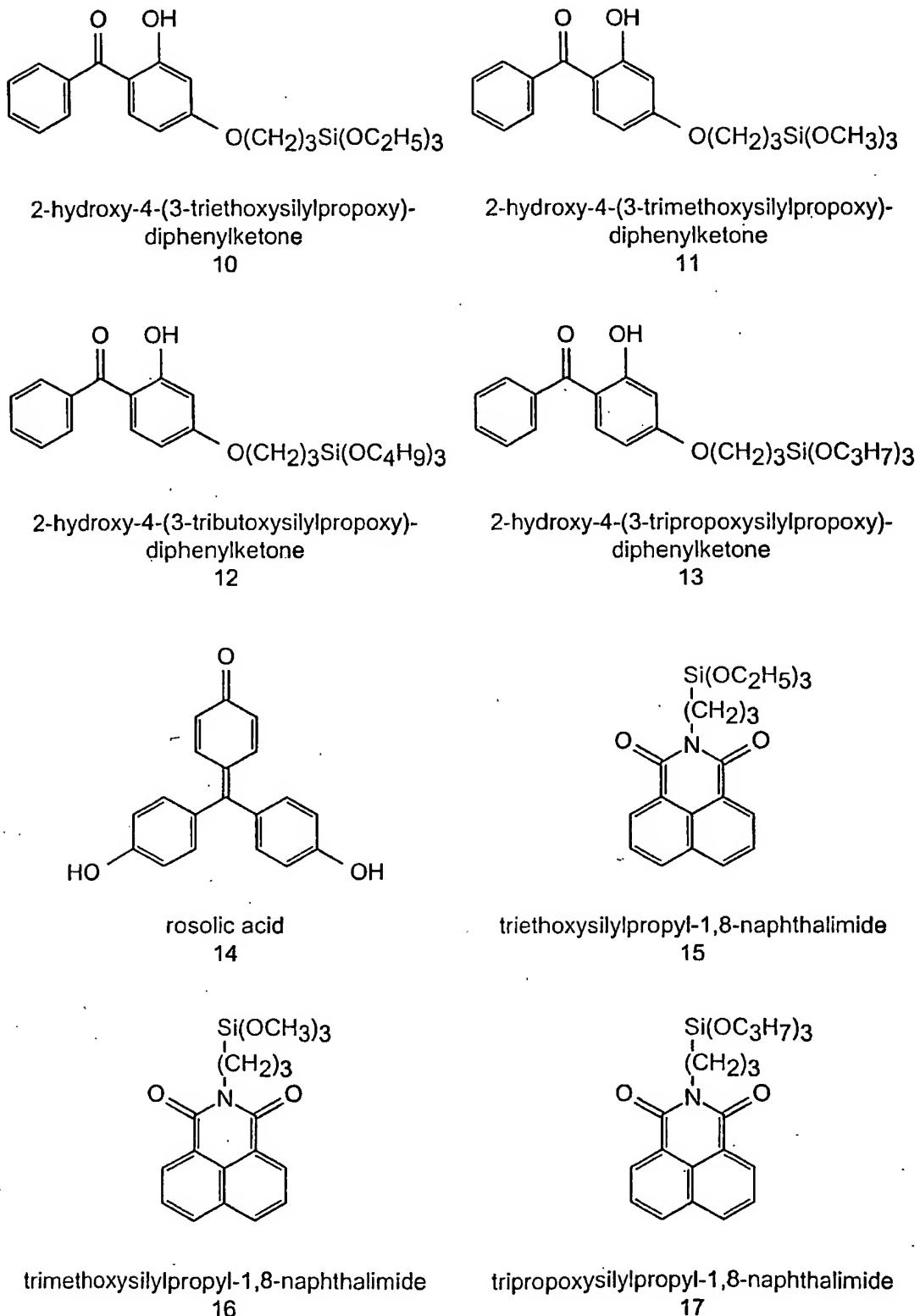


FIG. 1C

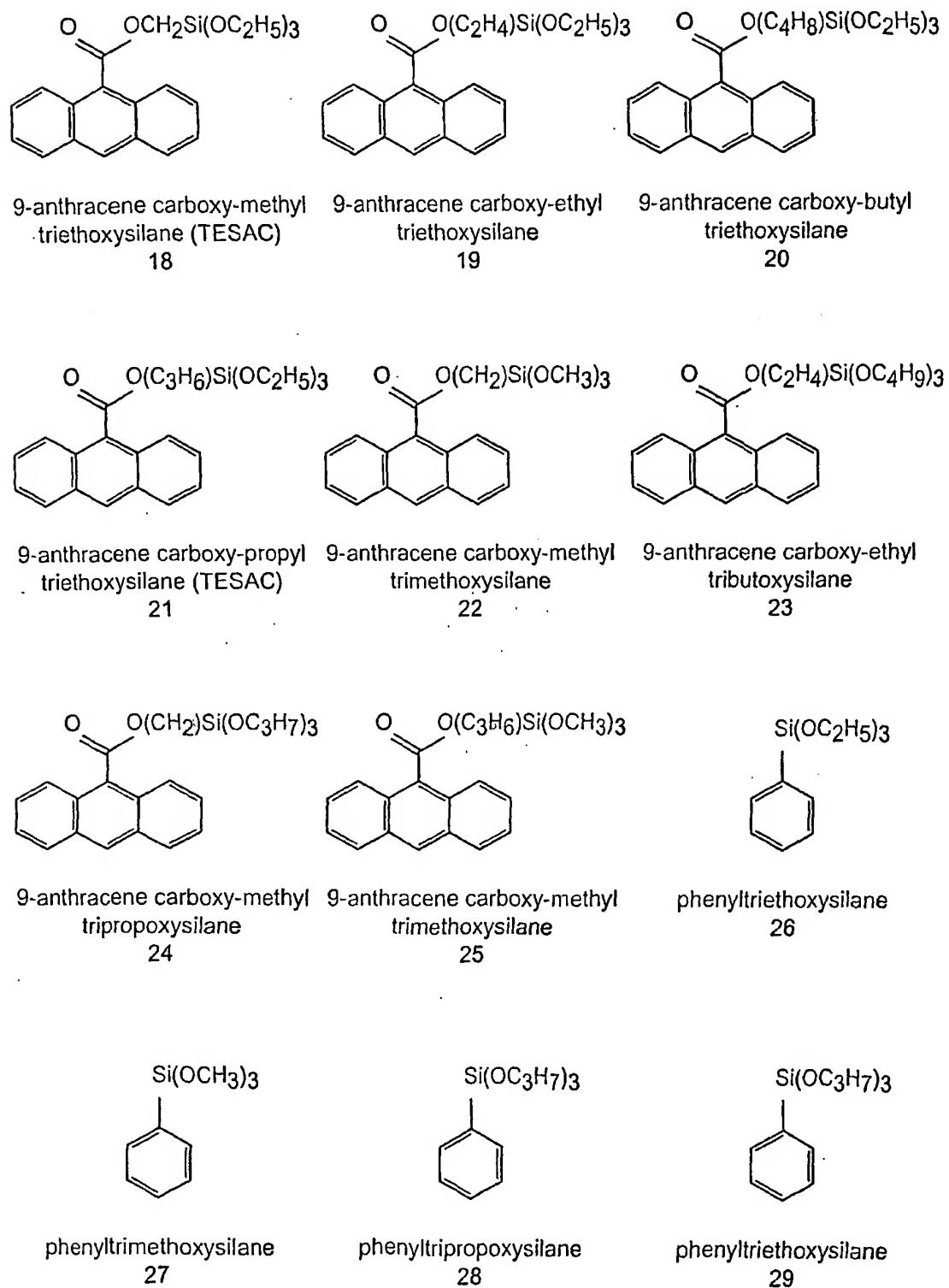
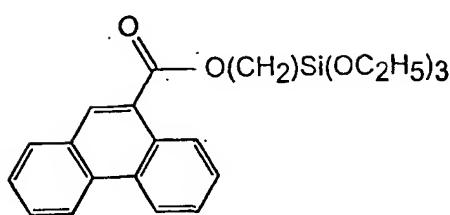
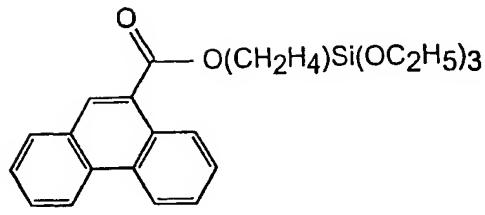


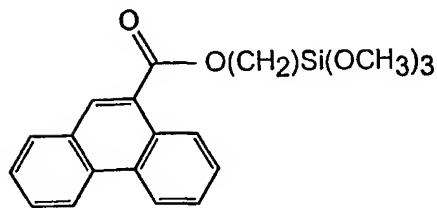
FIG. 1D



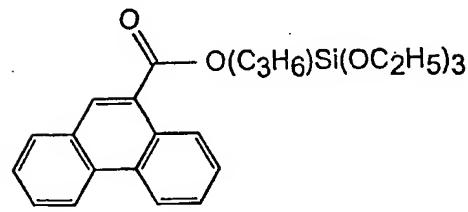
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29



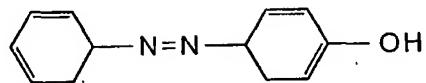
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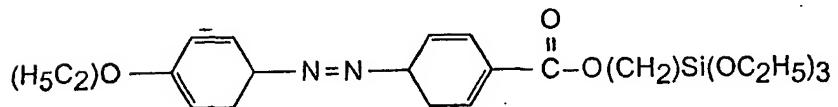
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trimethoxysilane
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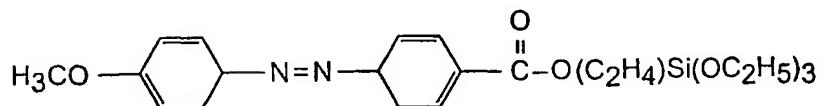
10-phenanthrene carboxy-propyl
triethoxysilane
32



4-phenylazophenol
33

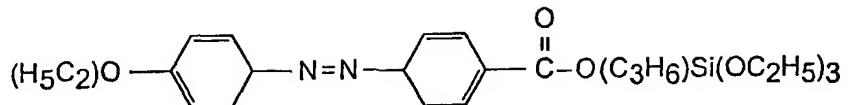


4-ethoxyphenylazobenzene-4-carboxy
methyl triethoxysilane
34



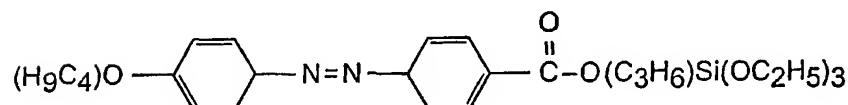
4-methoxyphenylazobenzene-4-carboxy
ethyl triethoxysilane
35

FIG. 1E



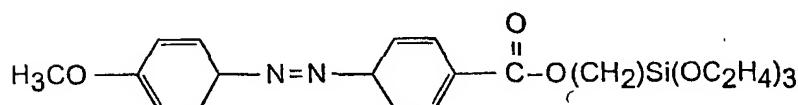
4-ethoxyphenylazobenzene-4-carboxy
propyl triethoxysilane

36



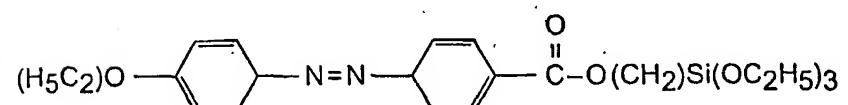
4butoxyphenylazobenzene-4-carboxy
propyl triethoxysilane

37



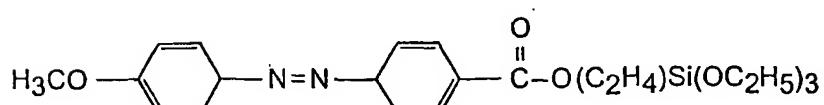
4-methoxyphenylazobenzene-4-carboxy
methyl triethoxysilane

38



4-ethoxyphenylazobenzene-4-carboxy
methyl triethoxysilane

39



4-methoxyphenylazobenzene-4-carboxy
ethyl triethoxysilane

40

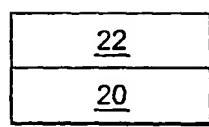


FIG. 2a

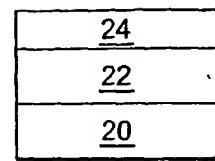


FIG. 2b

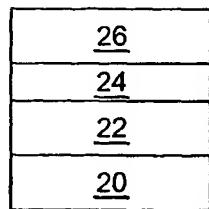


FIG. 2c

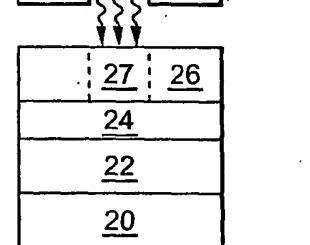


FIG. 2d

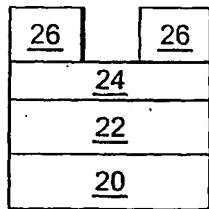


FIG. 2e

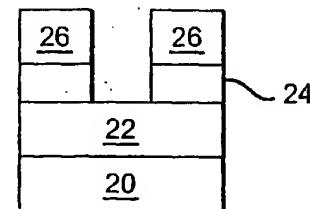


FIG. 2f

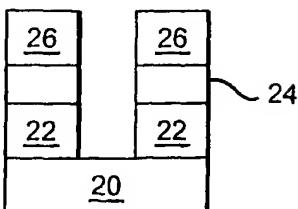


FIG. 2g

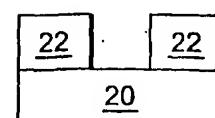


FIG. 2h

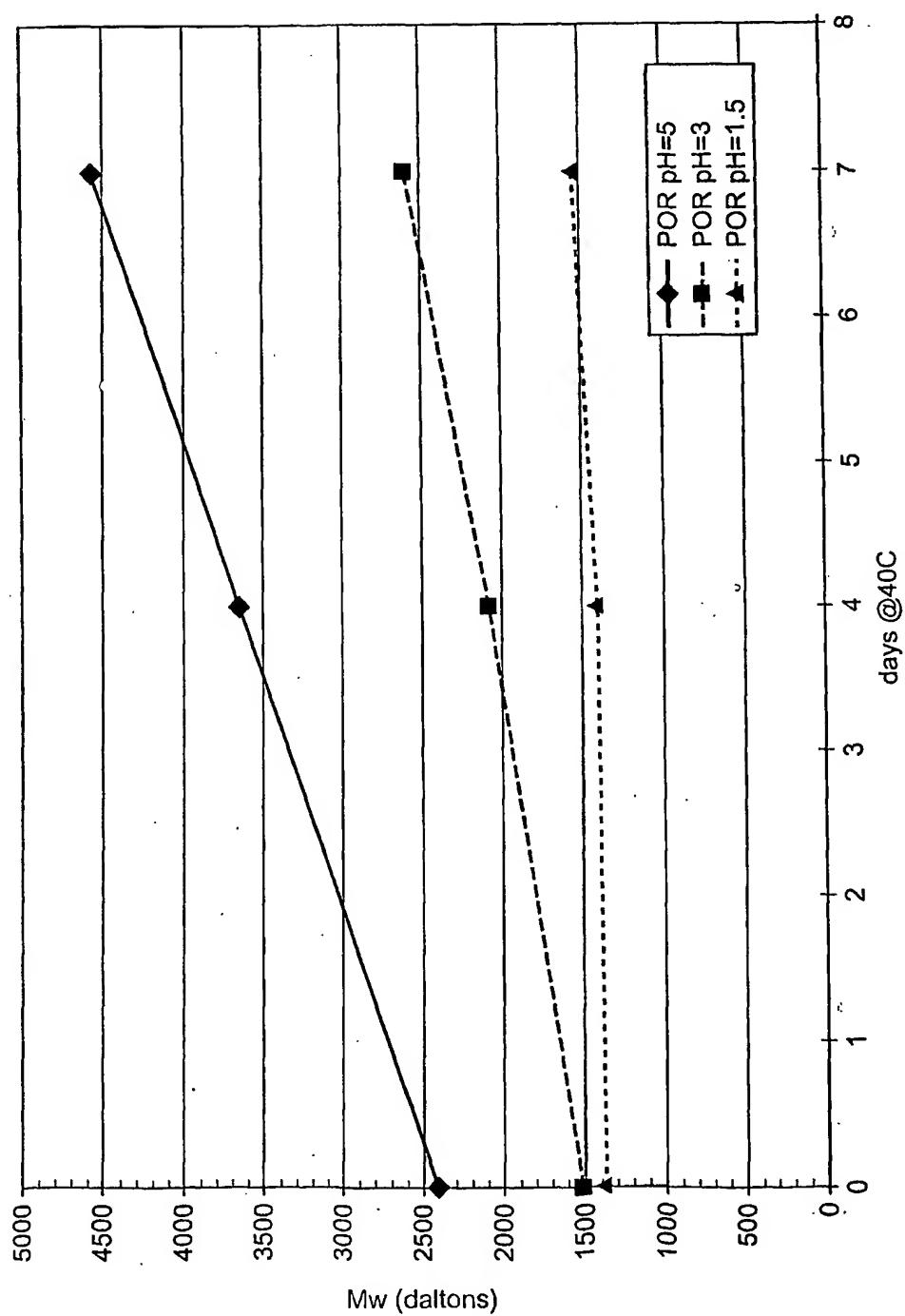
FIG. 3
POR Mw -- 40C Aging

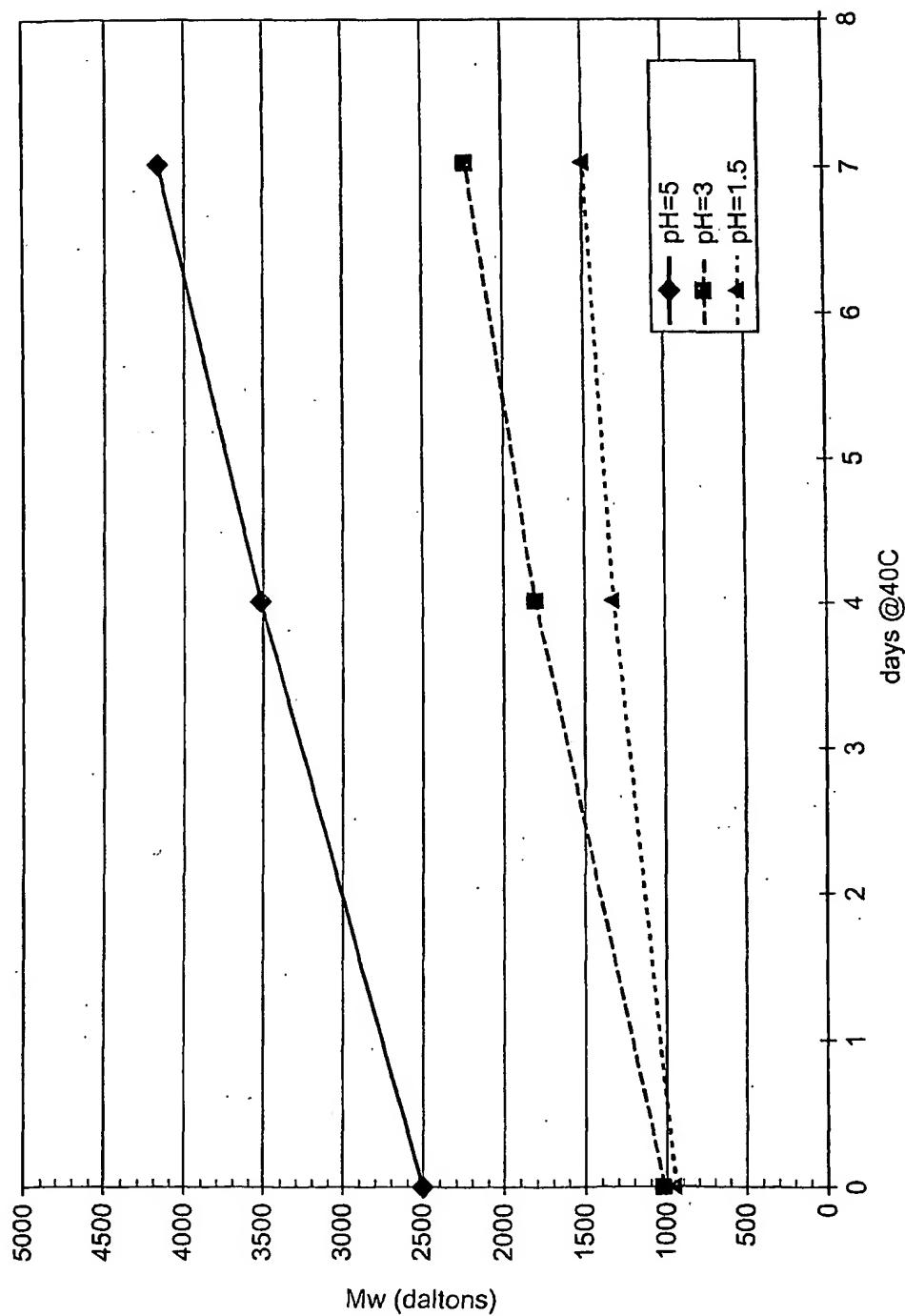
FIG. 4
2:1 EtOH/PGMEA Mw - 40c Aging

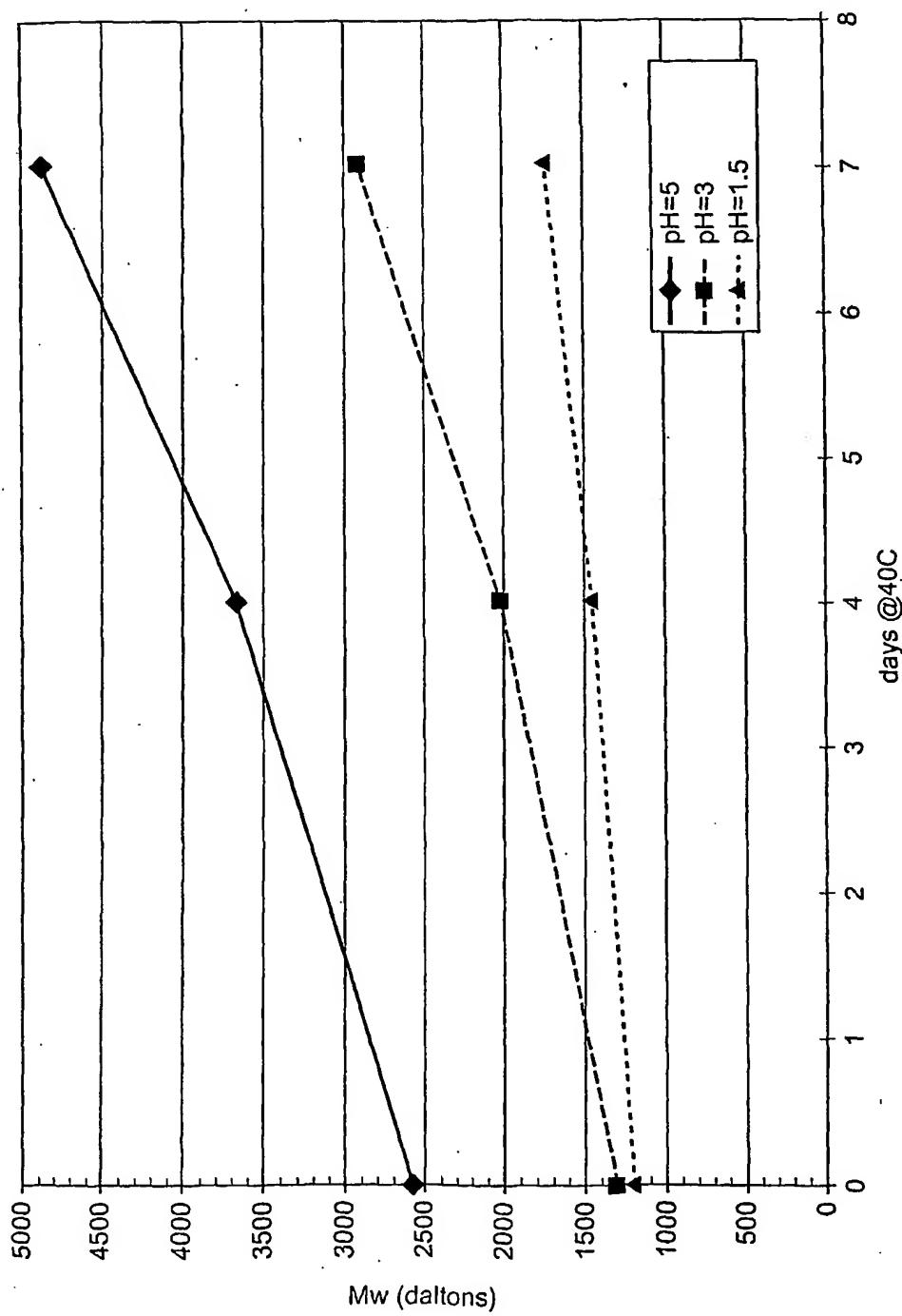
FIG. 5
2:1 PGMEA/EtOH Mw - 40C Aging

FIG. 6

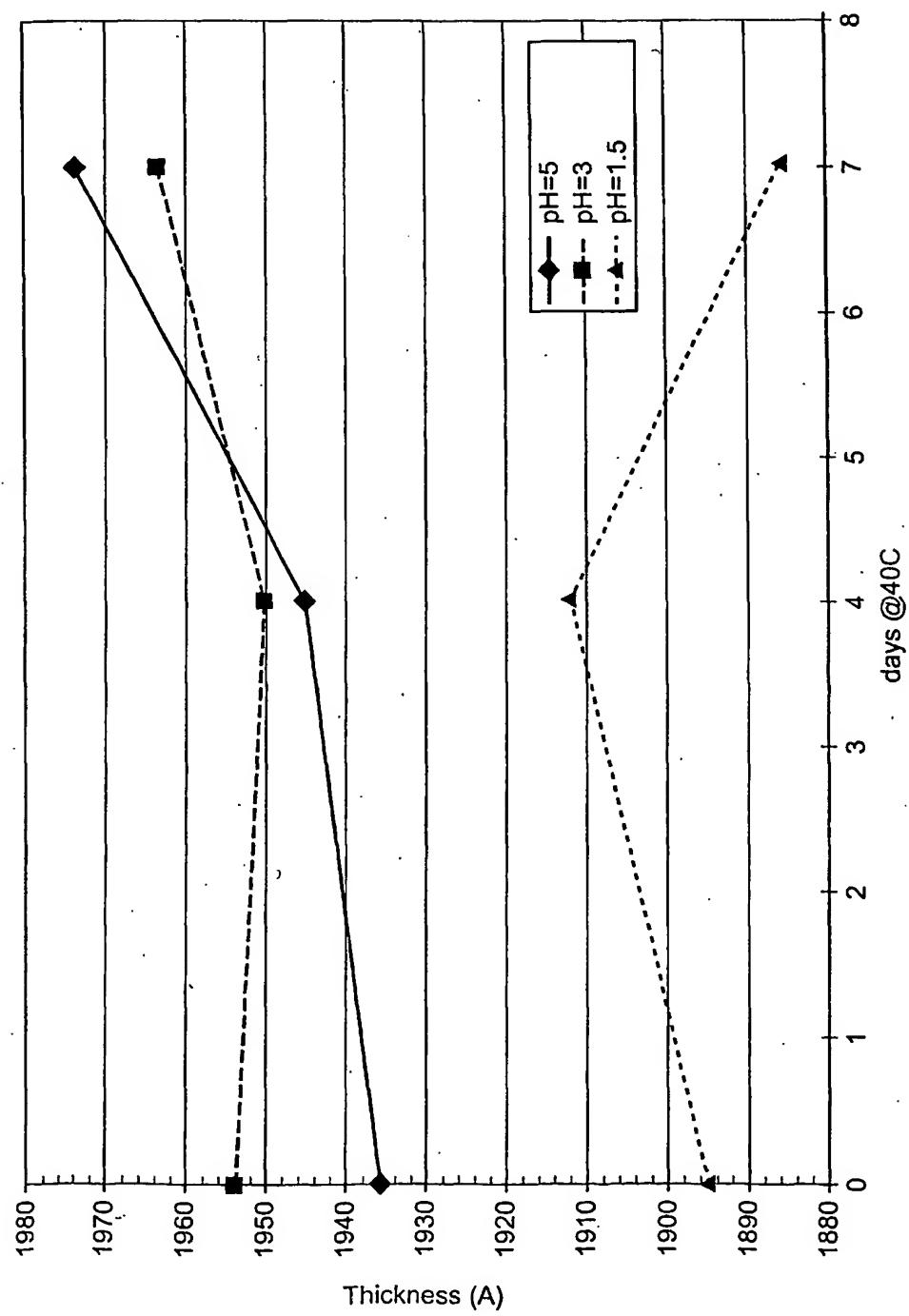


FIG. 7 2:1 EtOH/PGMEA Thickness -- 40C Aging

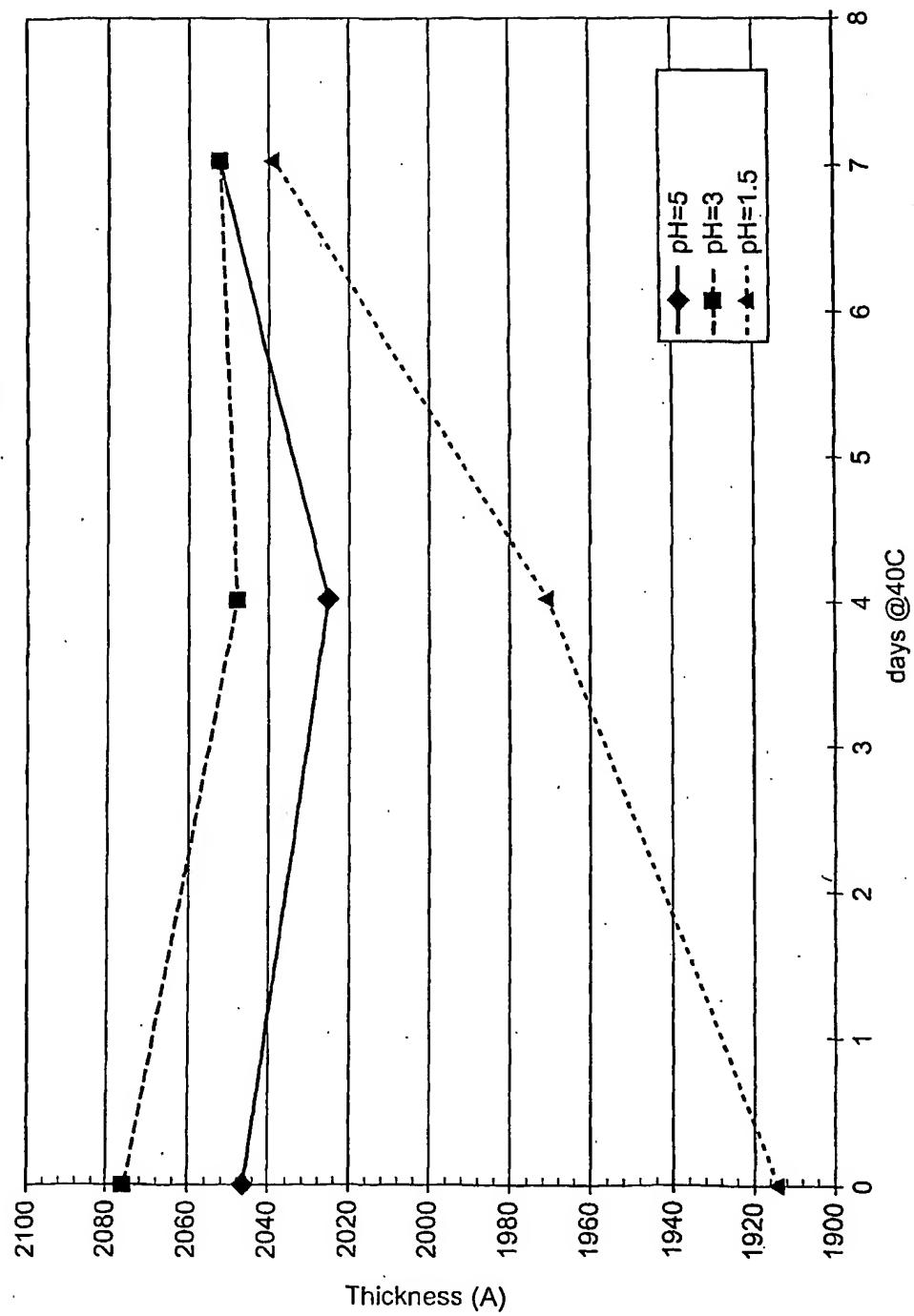


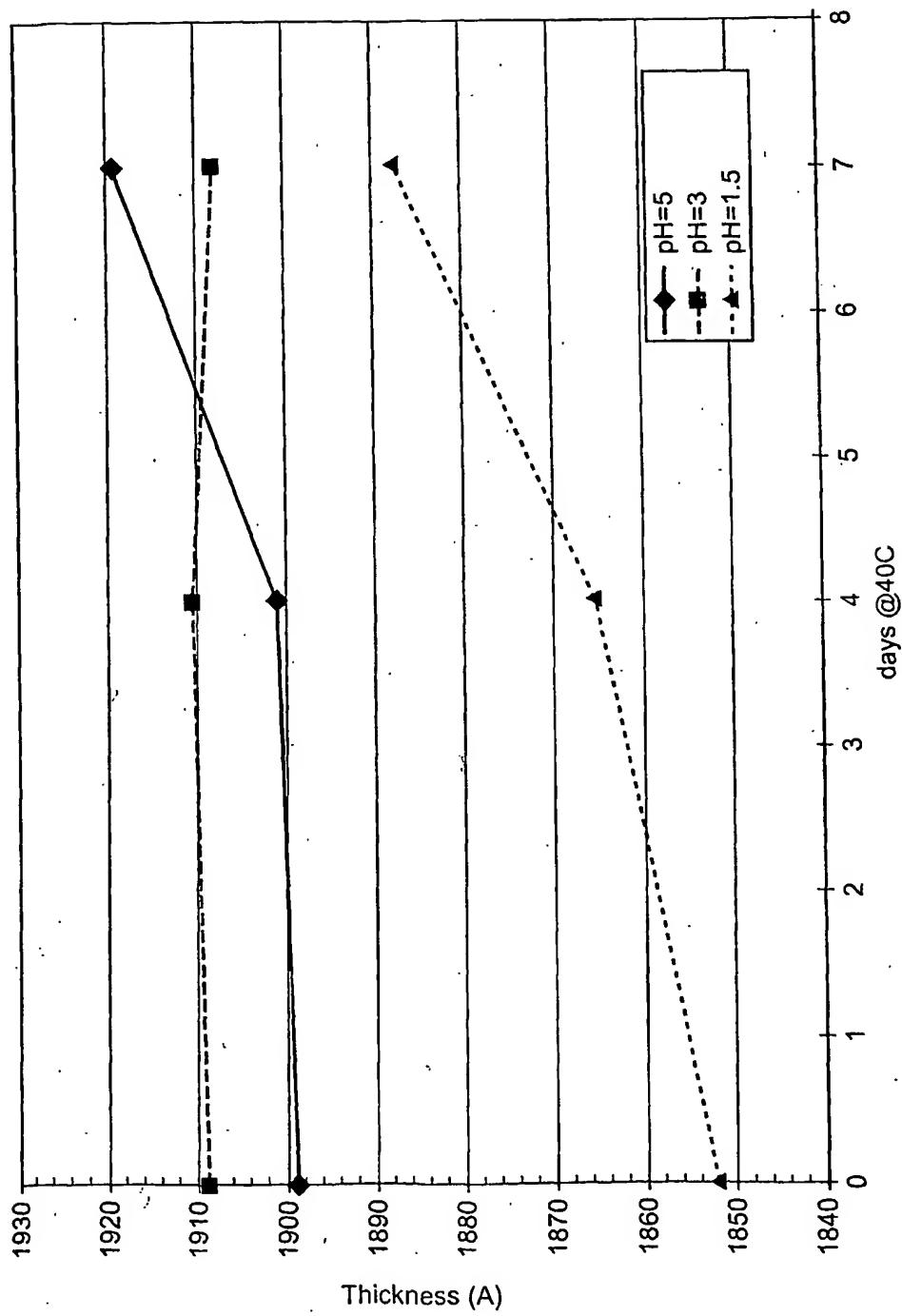
FIG. 8
2:1 PGMEA/EtOH Thickness -- 40C Aging

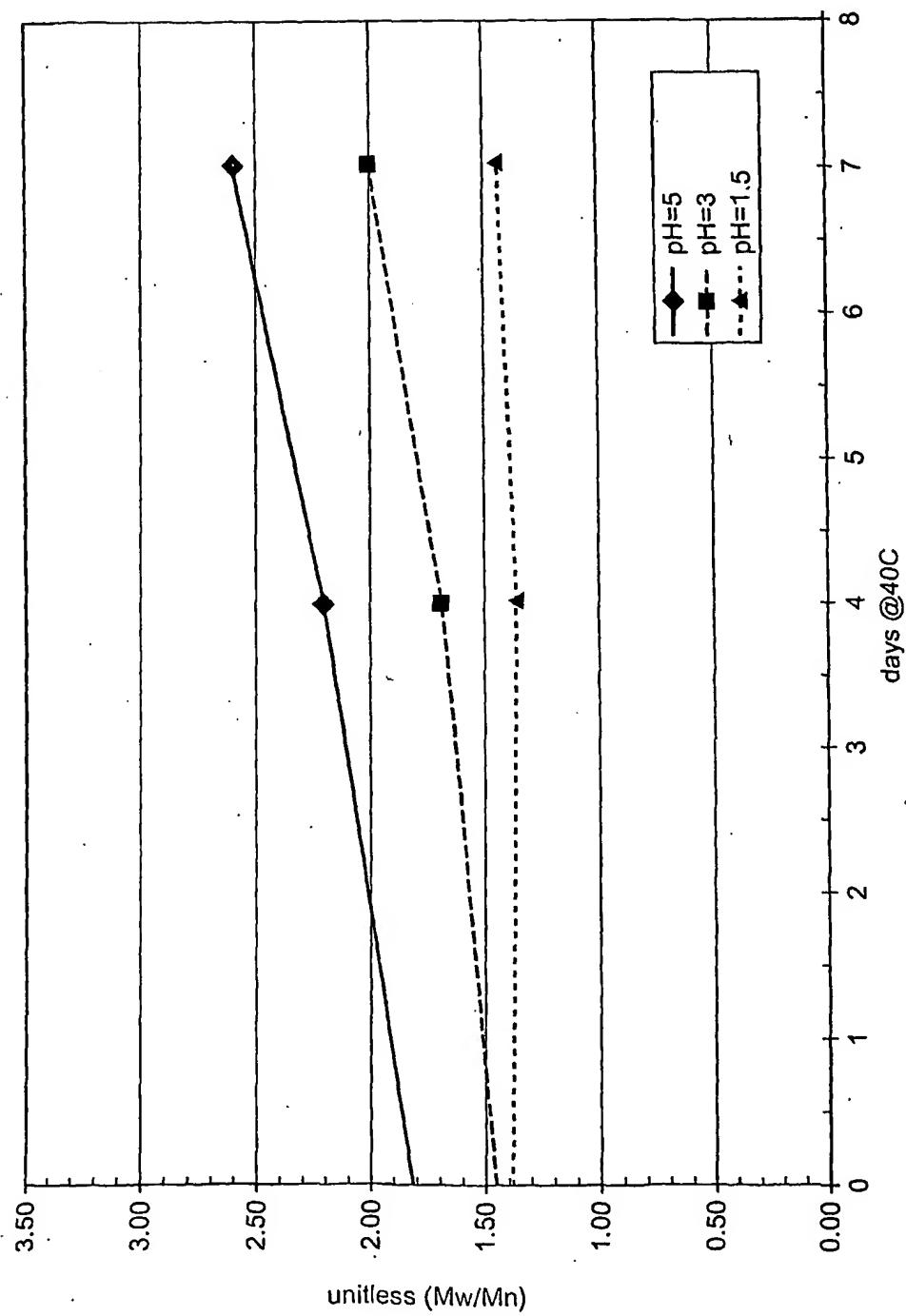
FIG. 9
POR MW Polydispersity -- 40C Aging

FIG. 10 2:1 EtOH/PGMEA MW Polydispersity - 40C Aging

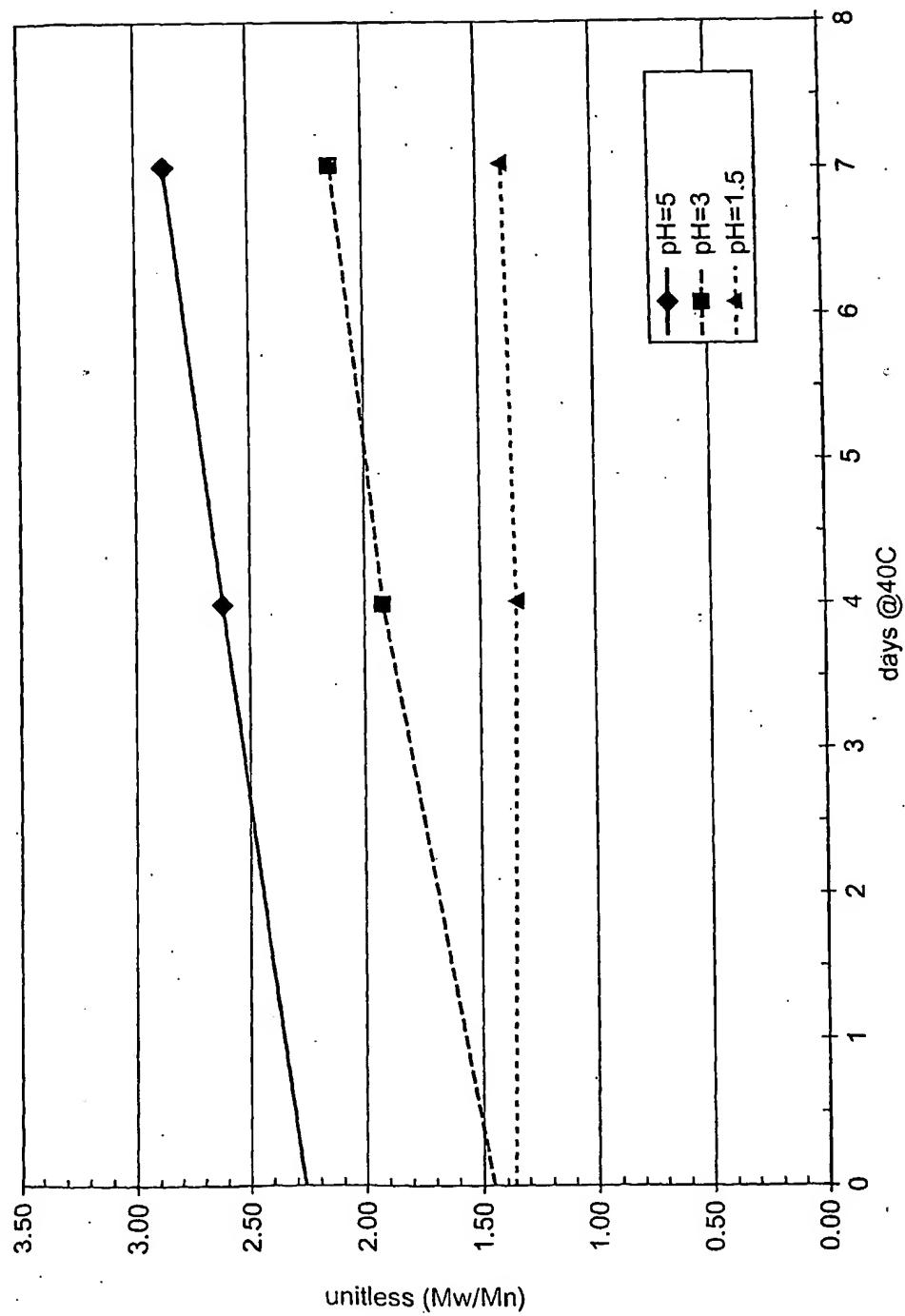


FIG. 11 2:1 PGMEA/EtOH MW Polydispersity - 40C Aging

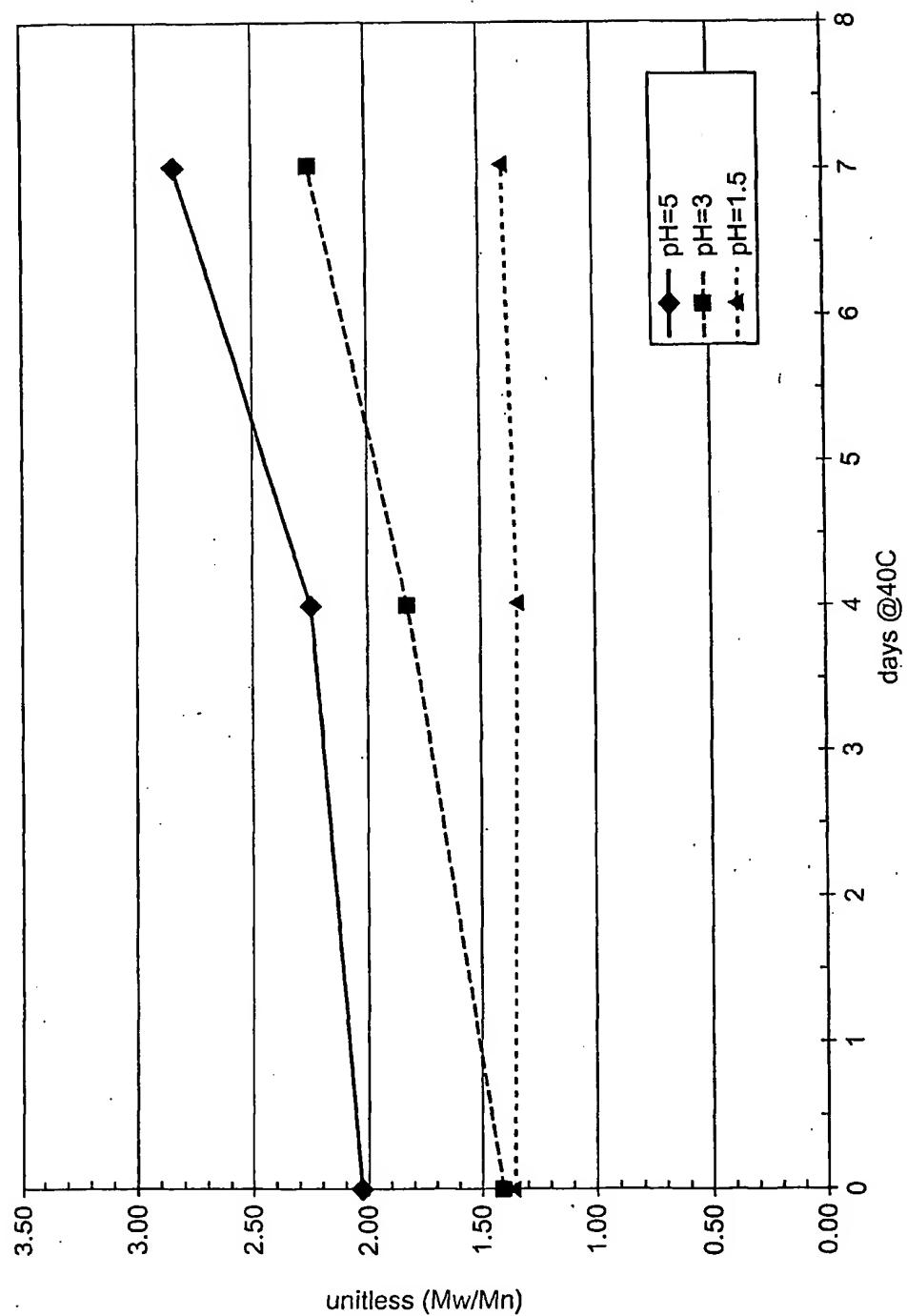
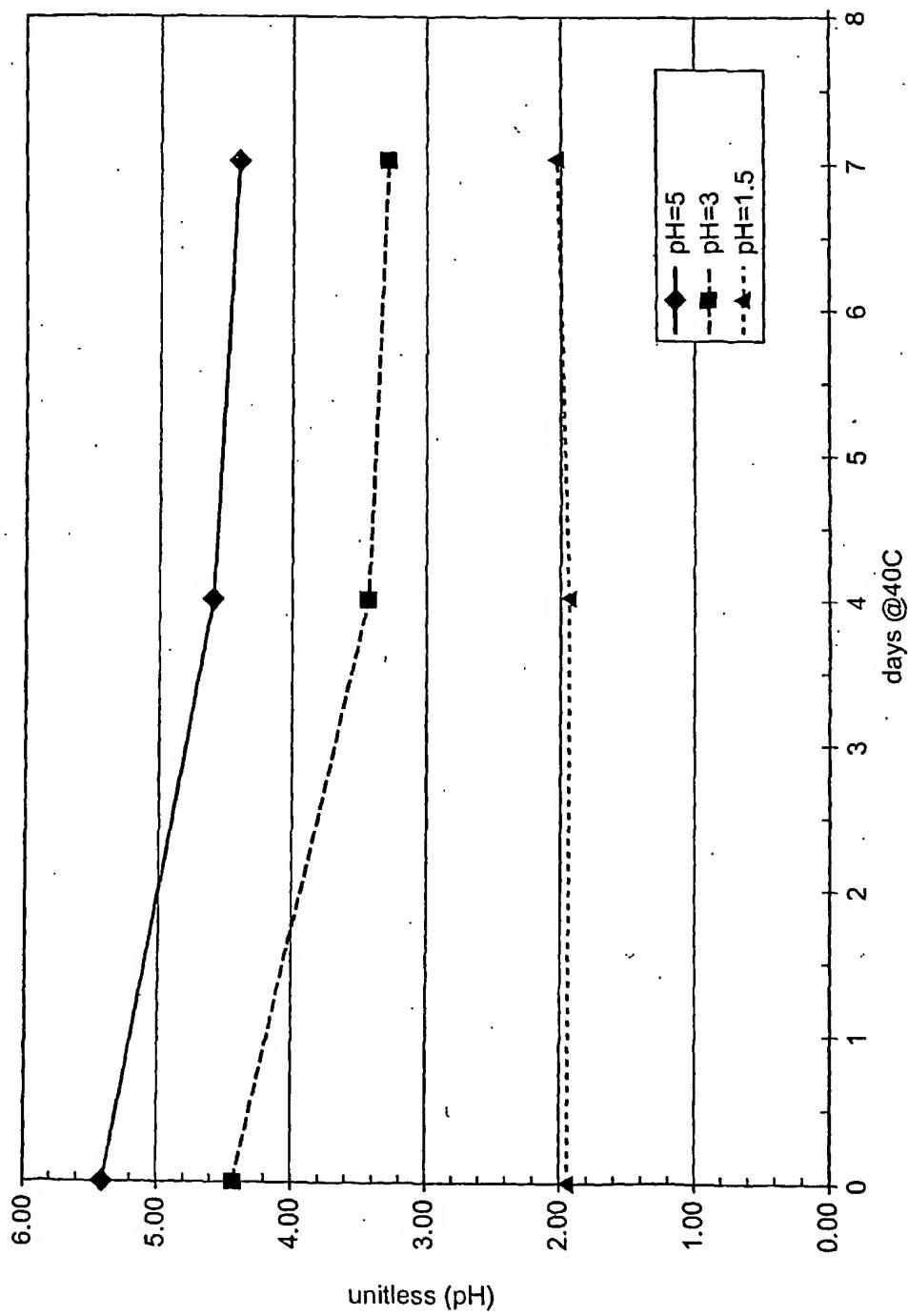


FIG. 12
POR pH Stability -- 40C Aging

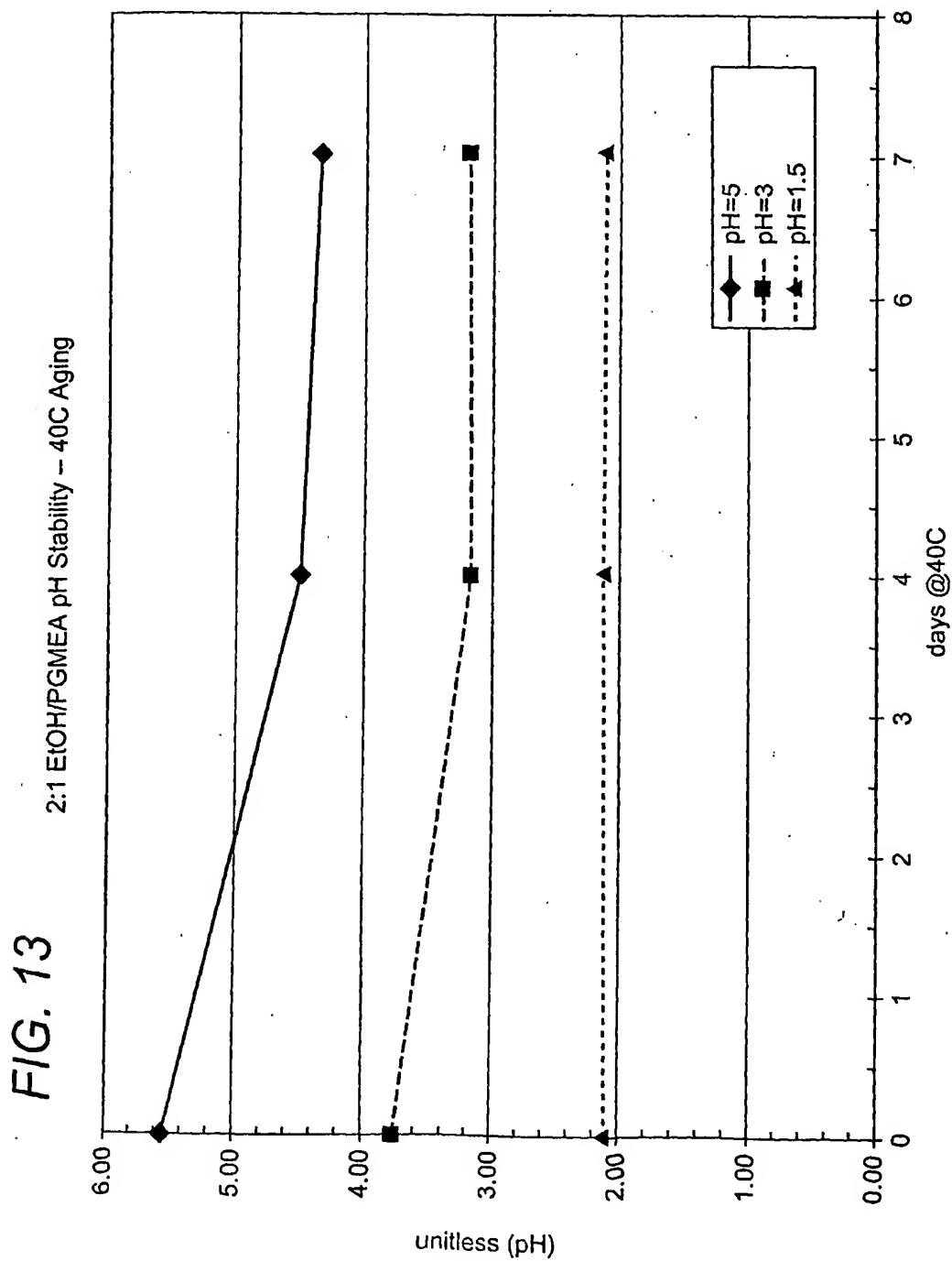
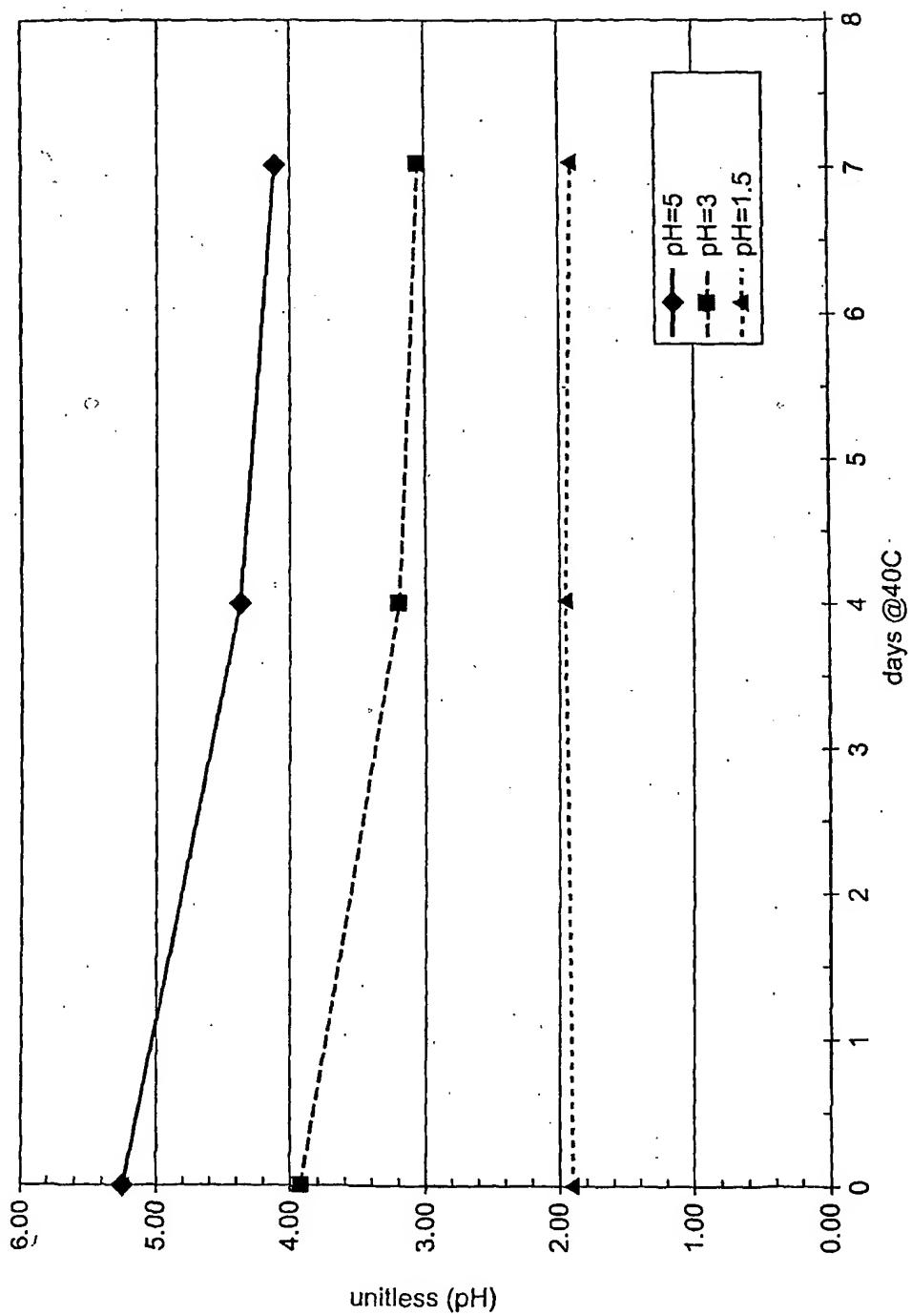


FIG. 14
2:1 PGMEA/EtOH pH Stability -- 40C Aging



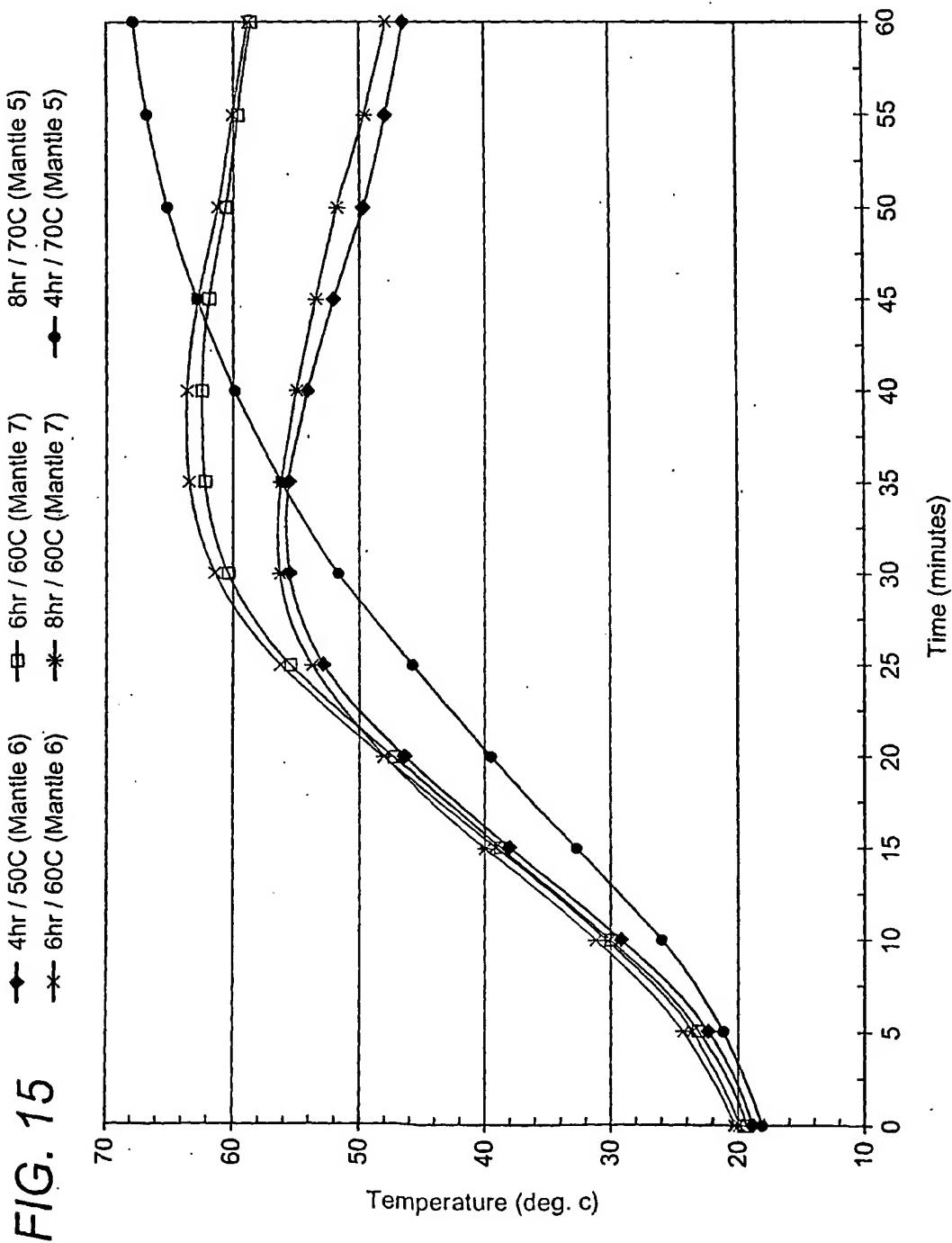


FIG. 16
 POR pH=1.5: % Via Fill for Pitch = 2 x Diameter
 as function of film thickness & via diameter

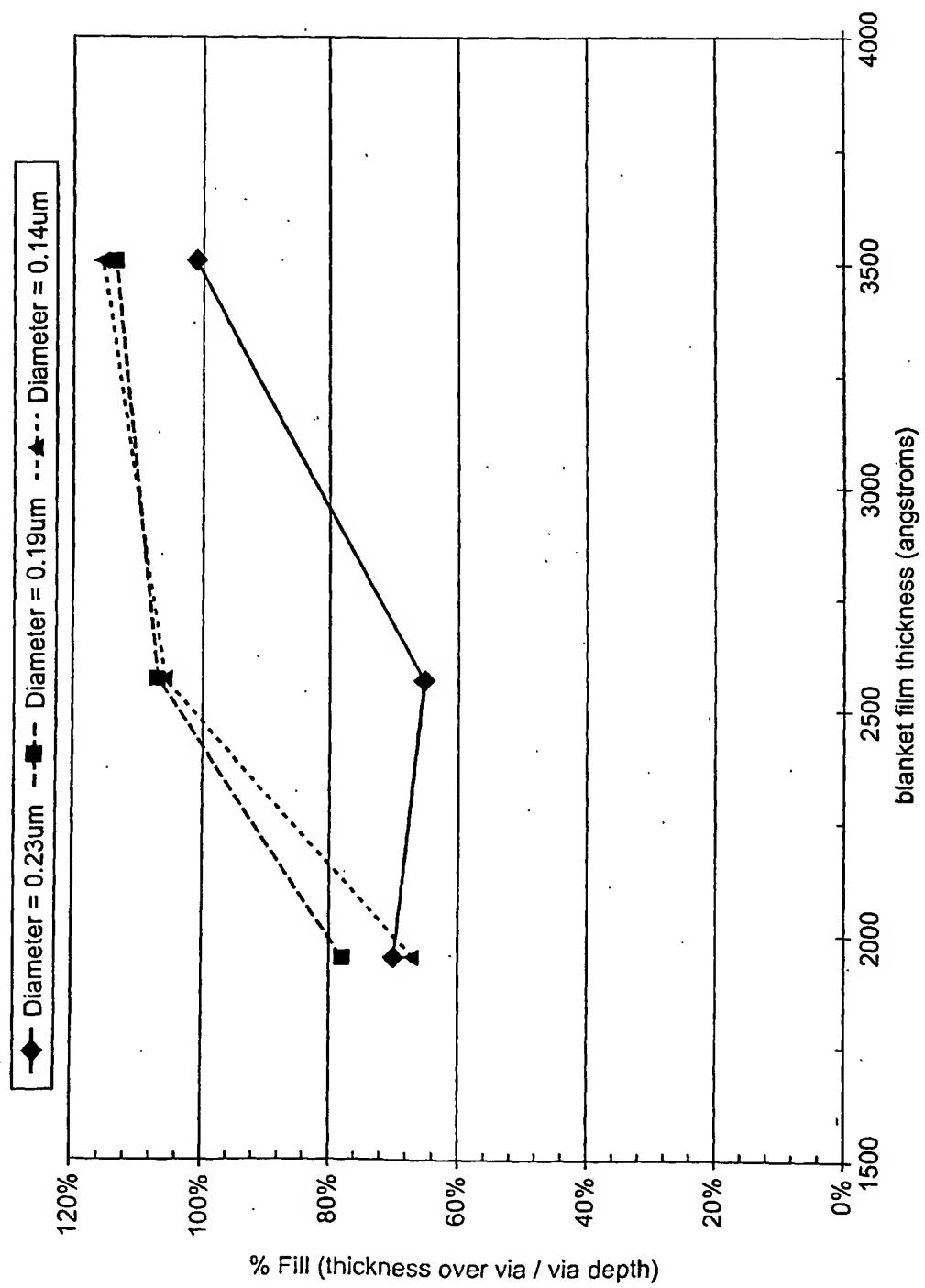


FIG. 17
POR pH=1.5, with high bp solvent: = % Via Fill for Pitch = 2x Diameter
 as function of film thickness & via diameter

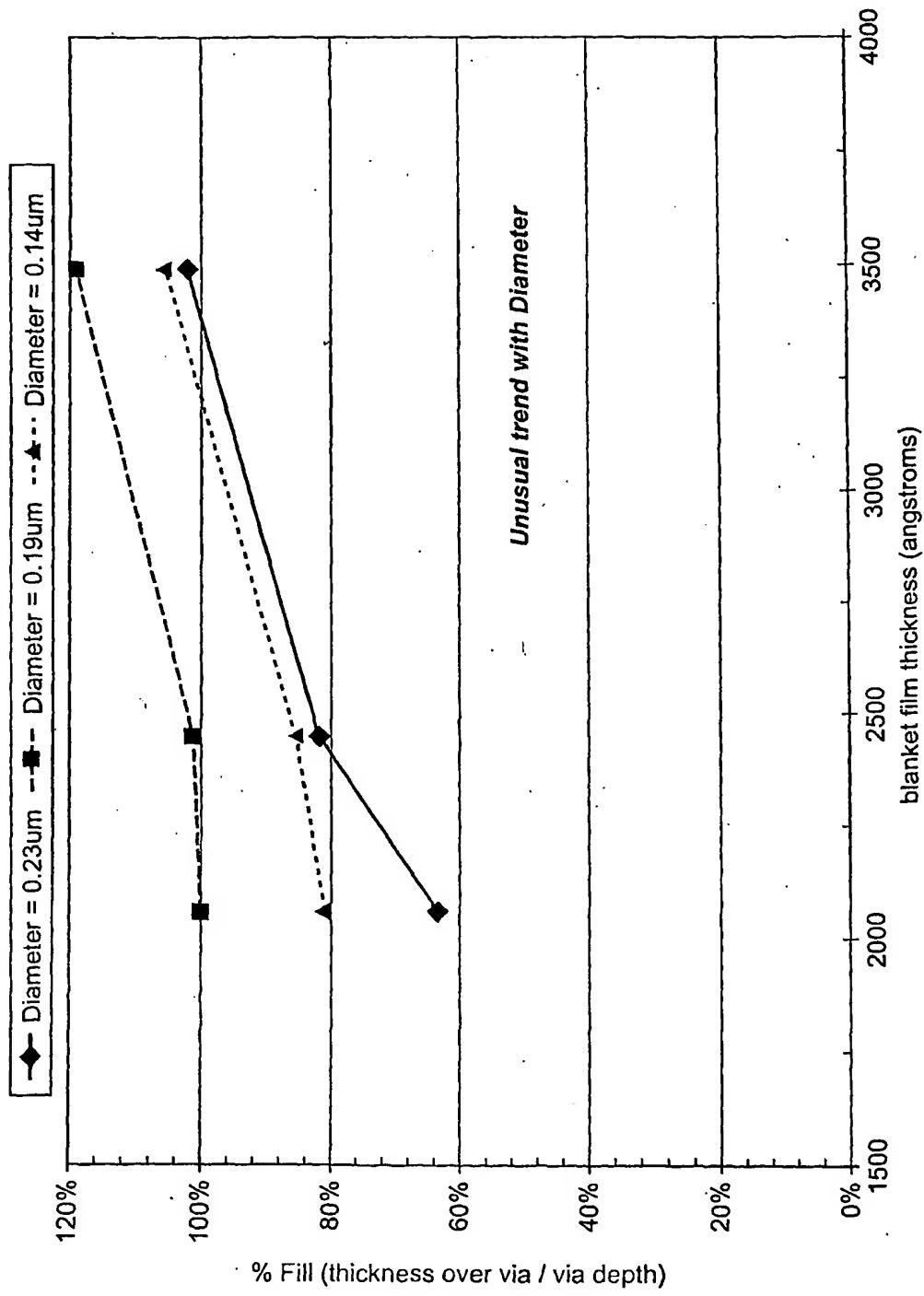


FIG. 18
POR: % Via Fill for Pitch = 2 x Diameter
 as function of film thickness & via diameter

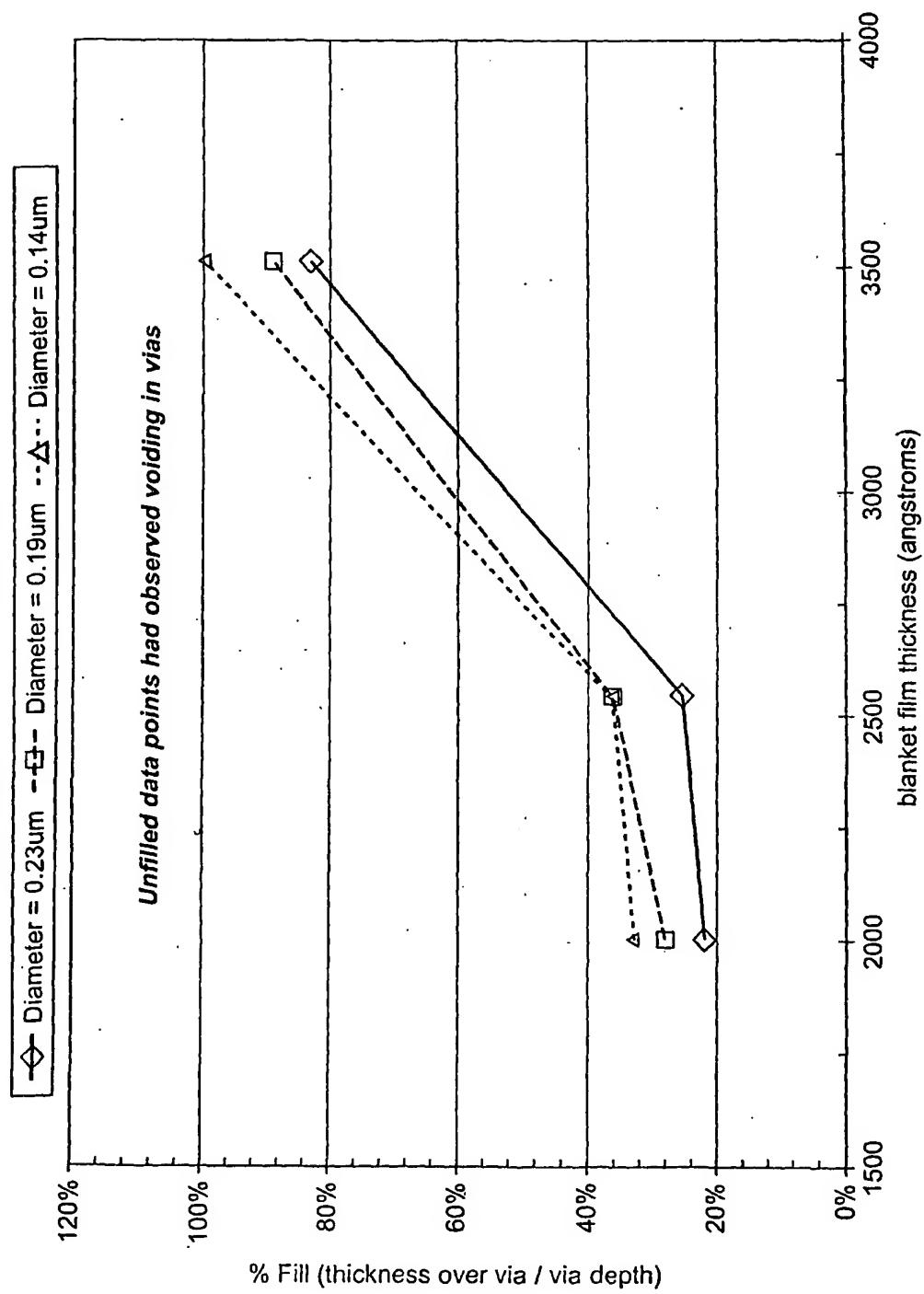


FIG. 19

POR with high bp solvent: % Via Fill for Pitch = 2 x Diameter
as function of film thickness & via diameter

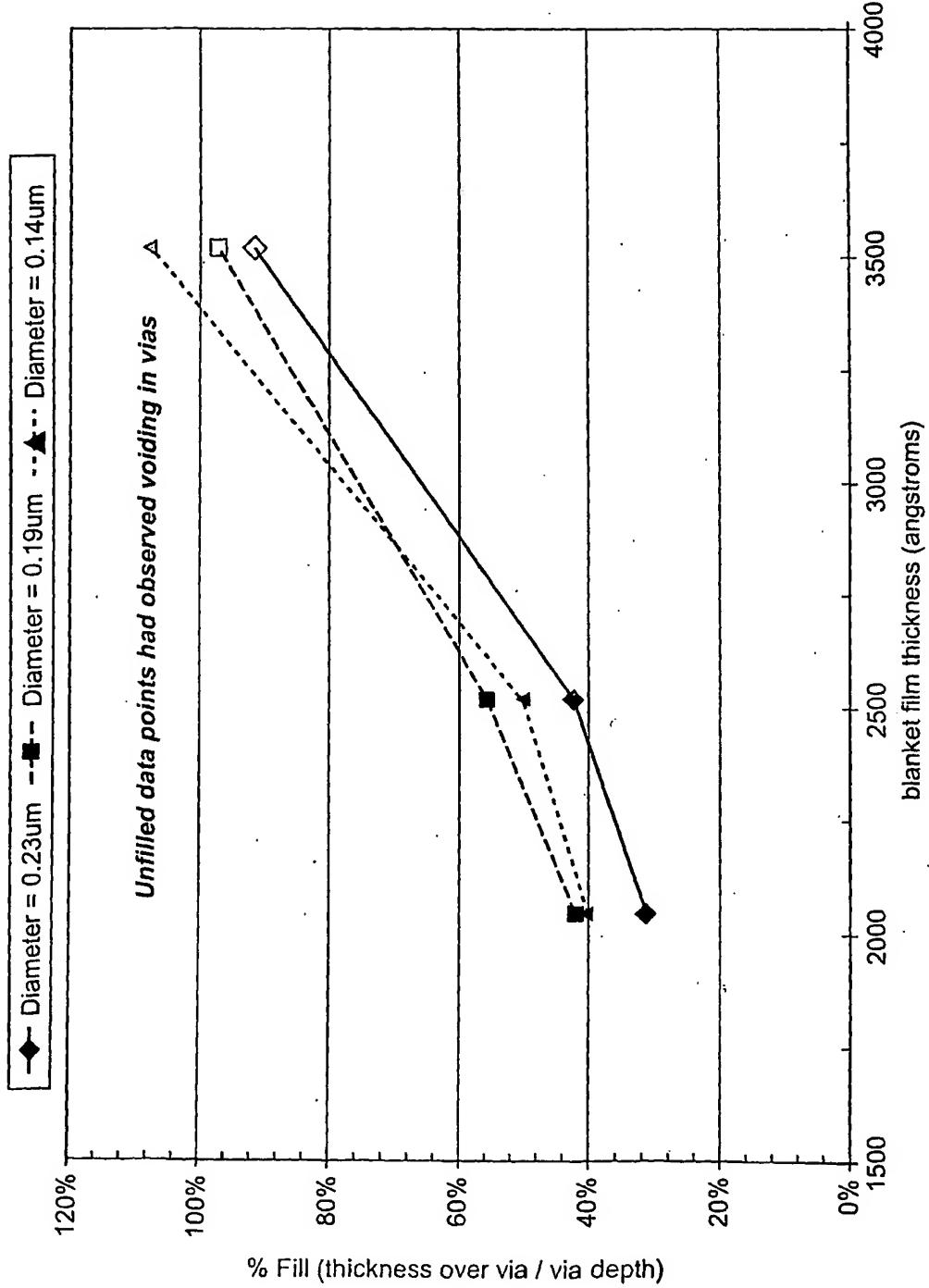


FIG. 20

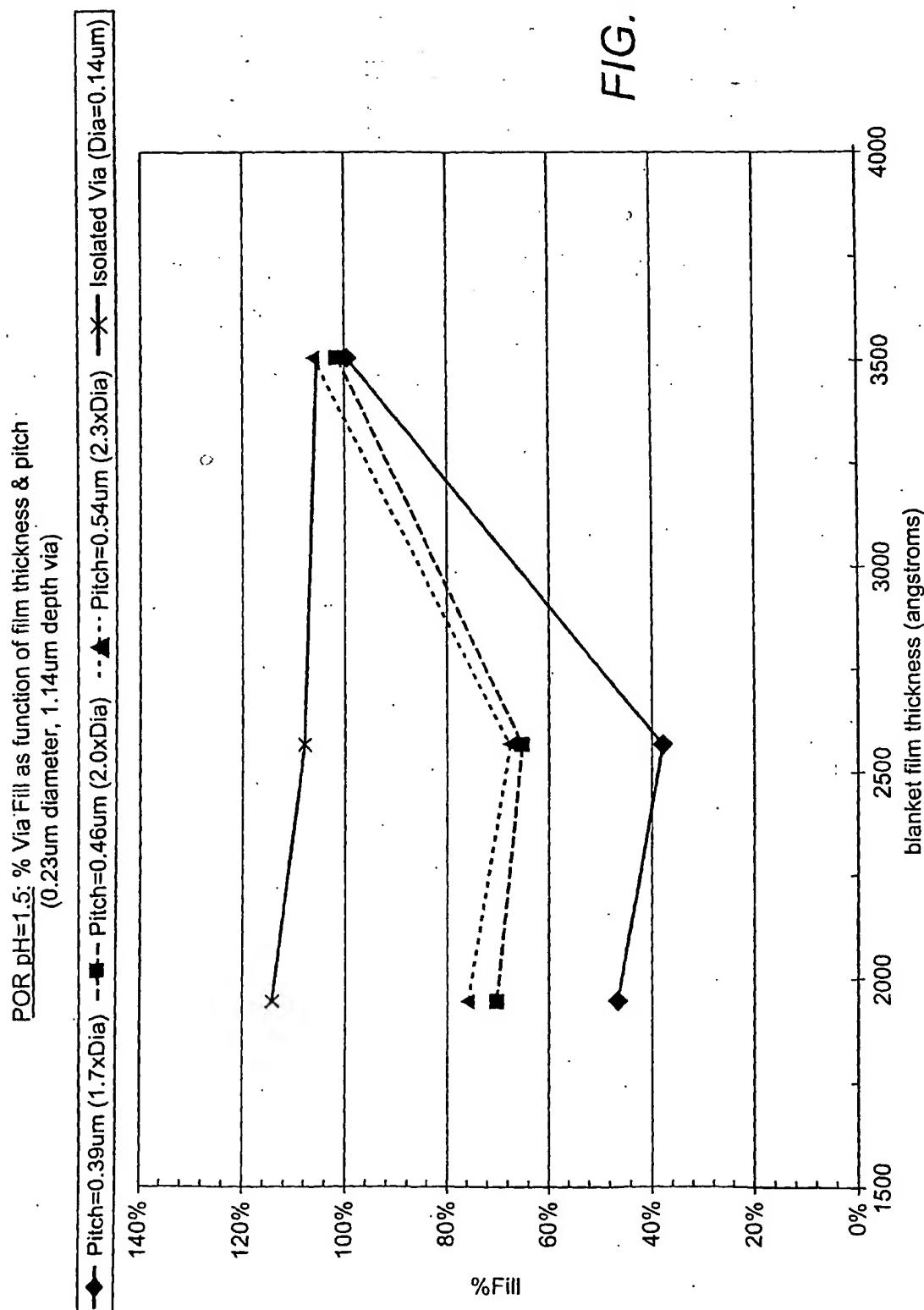


FIG. 21

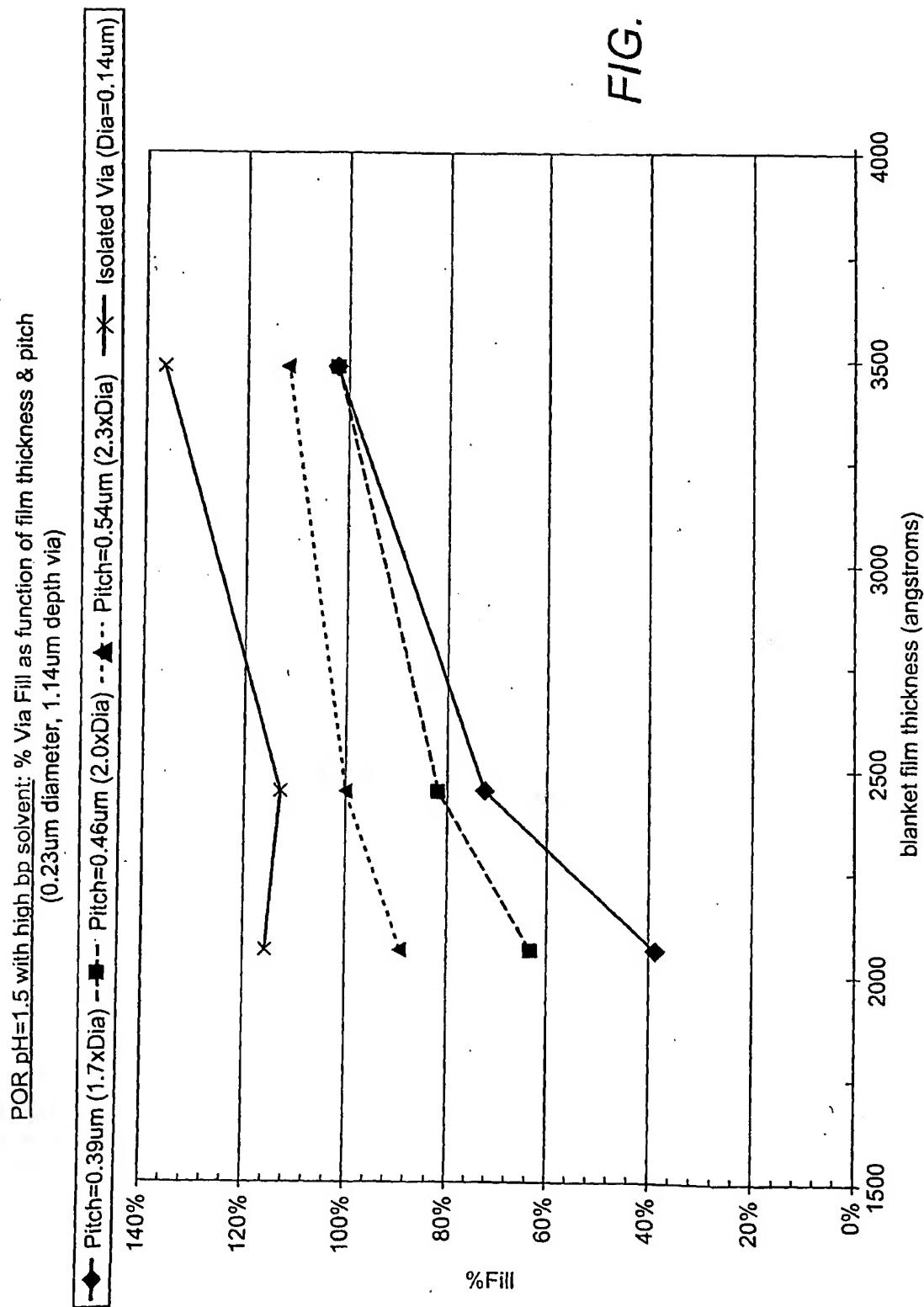


FIG. 22

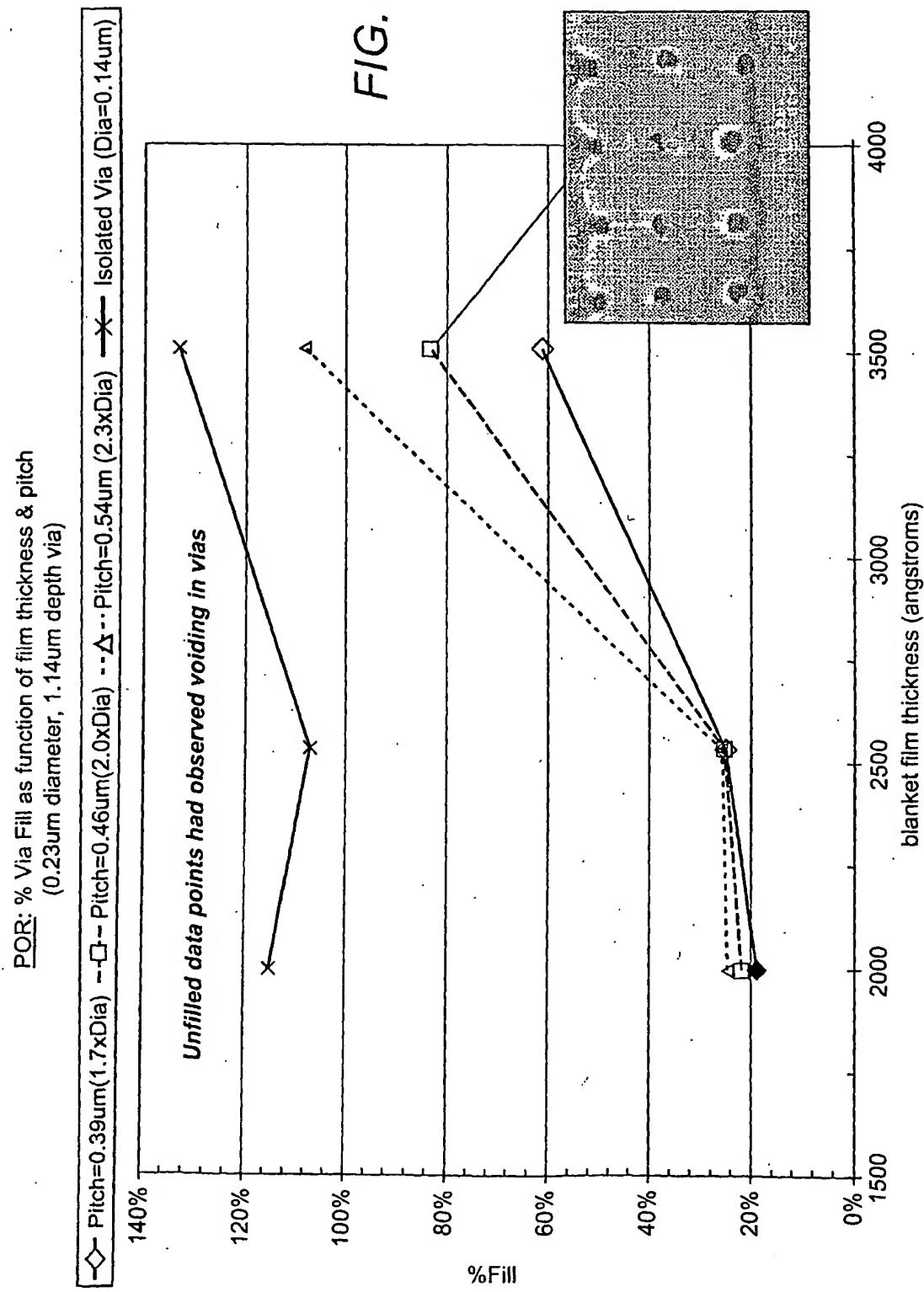


FIG. 23

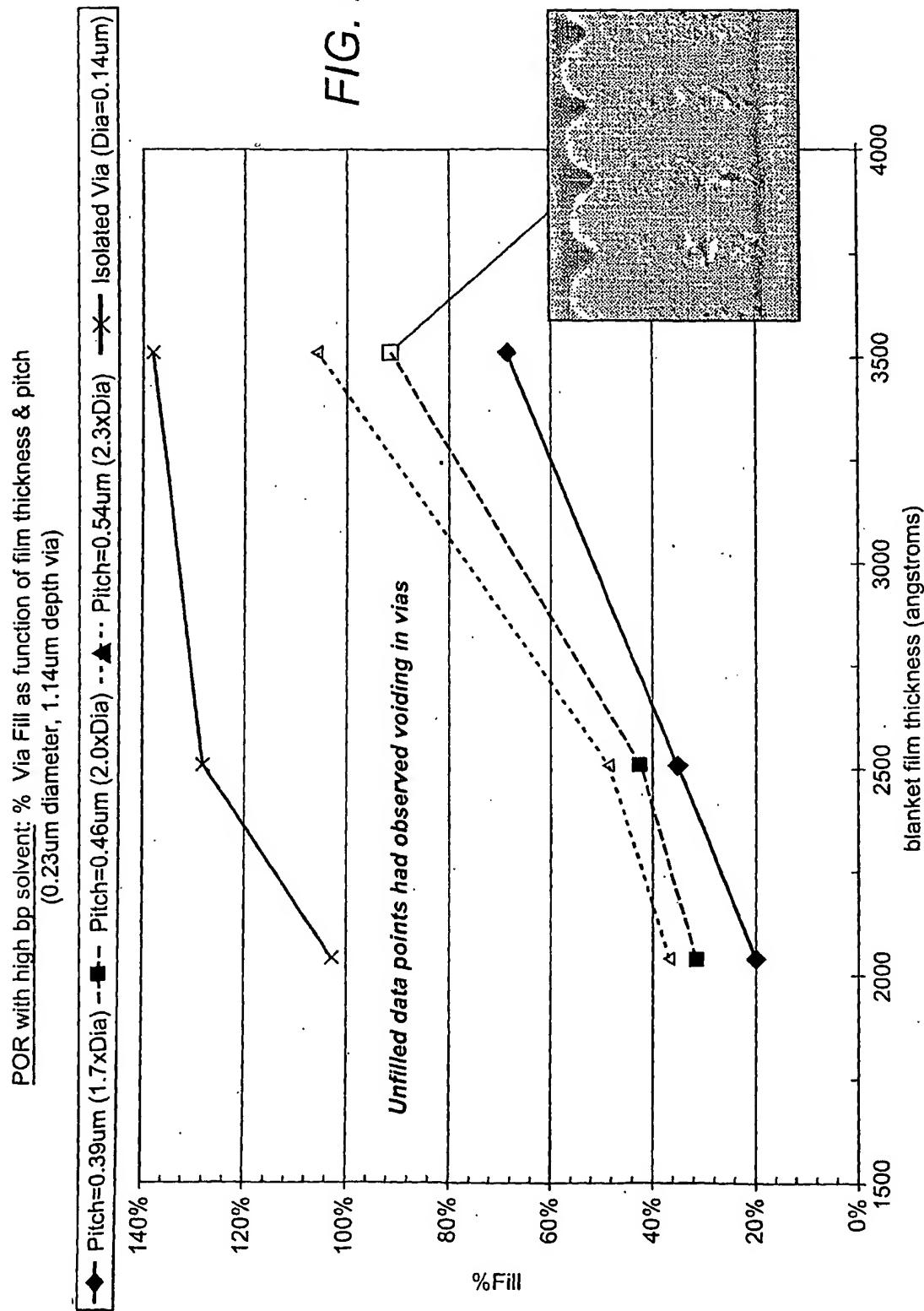


FIG. 24

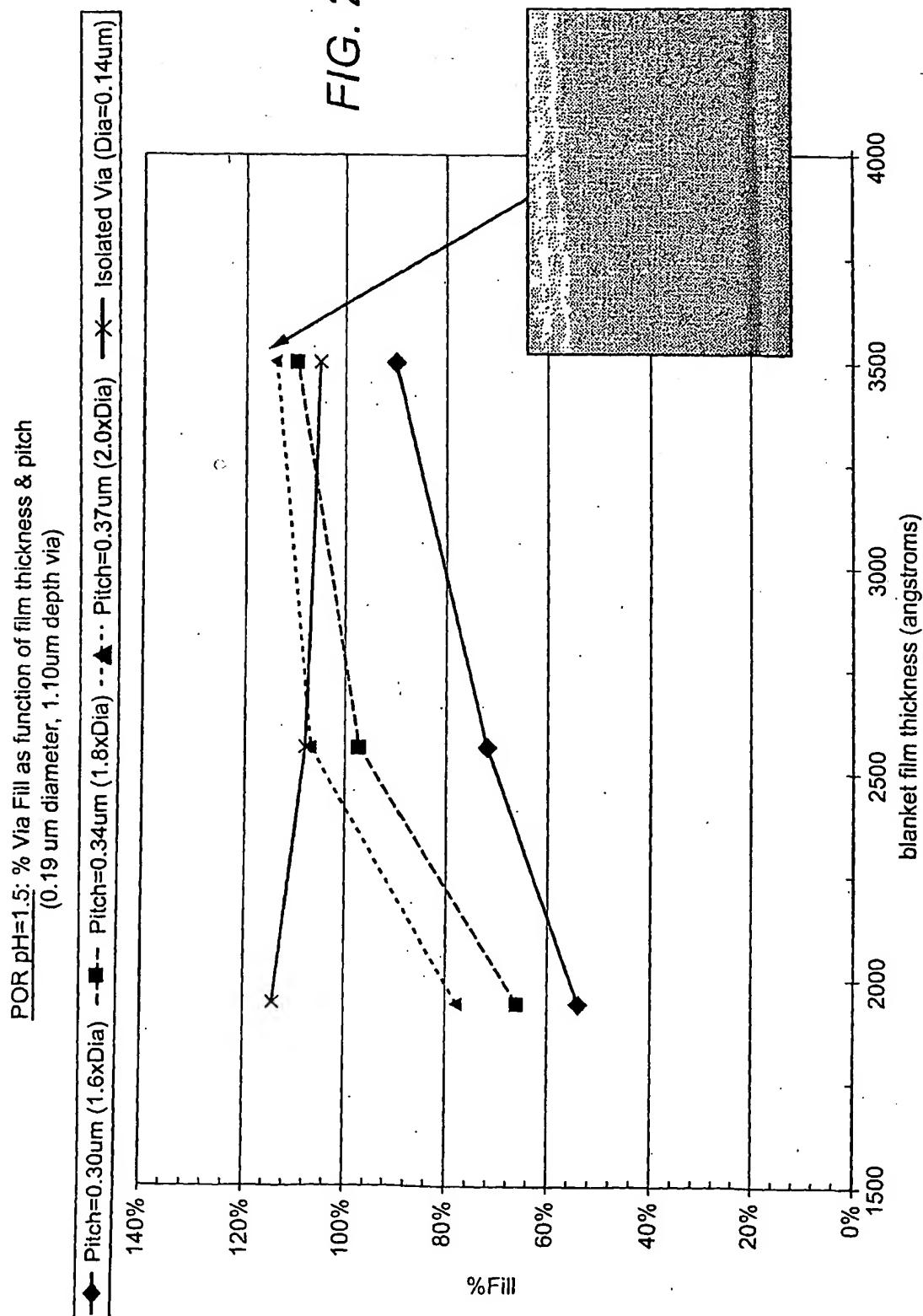


FIG. 25

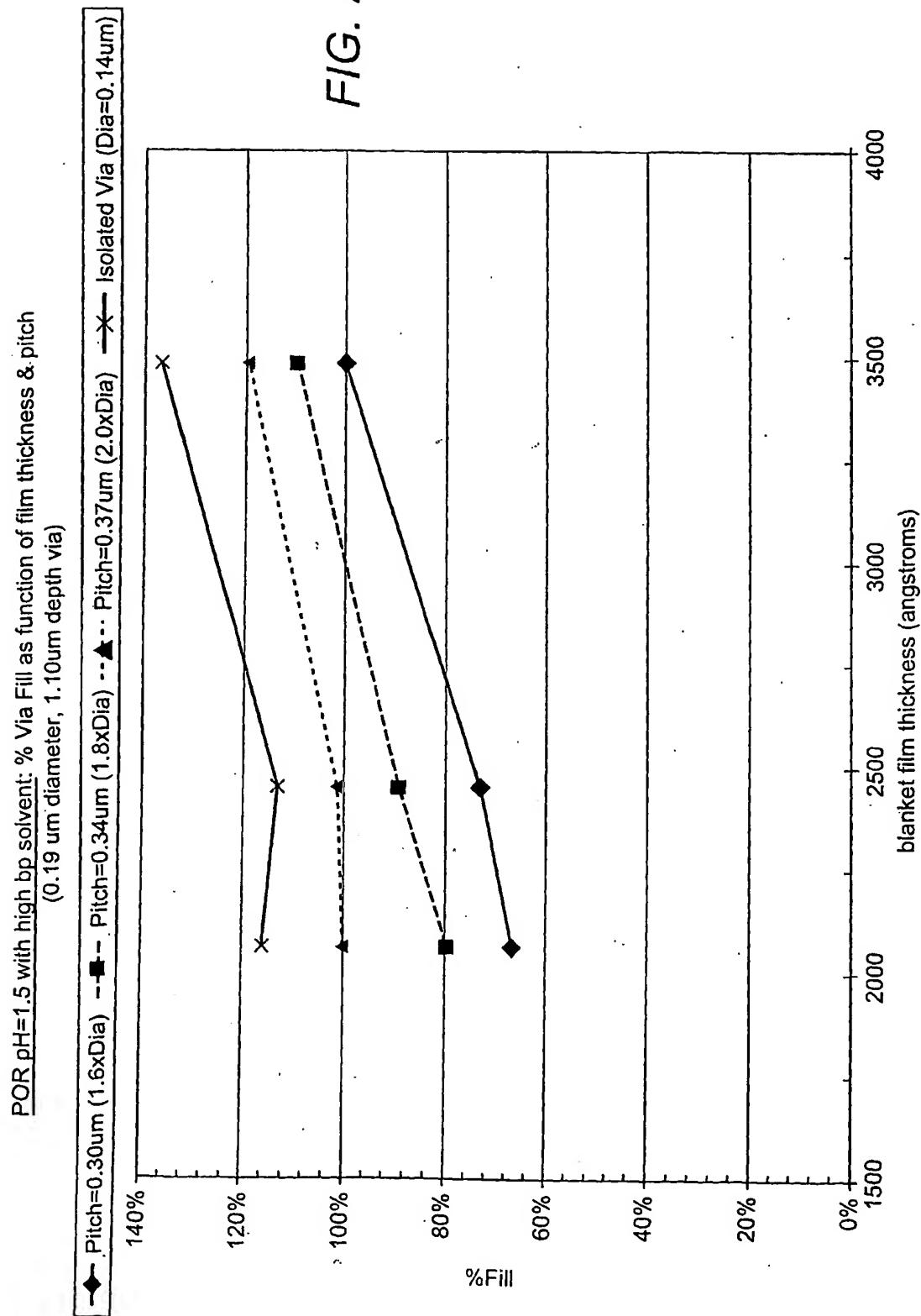


FIG. 26

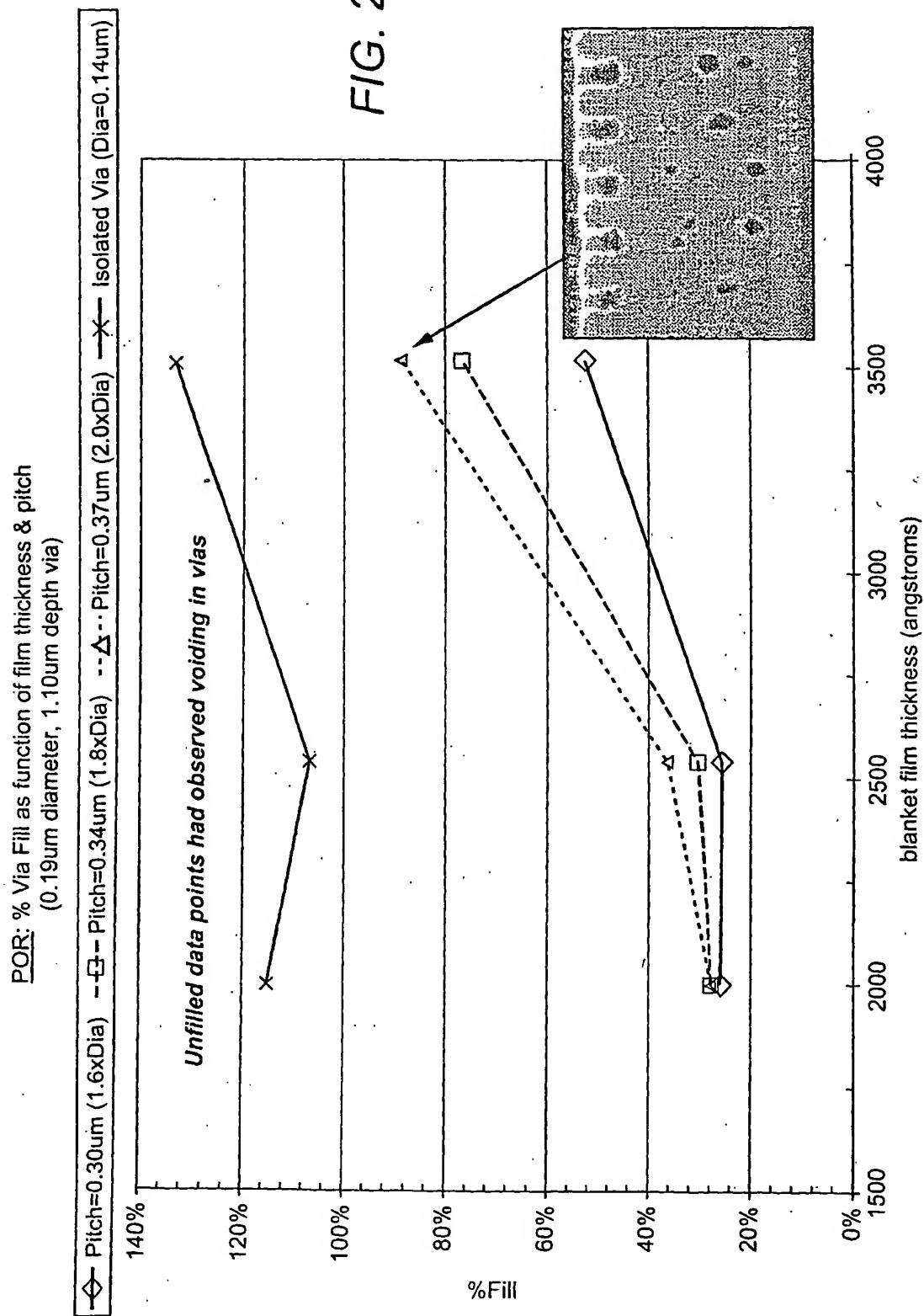


FIG. 27

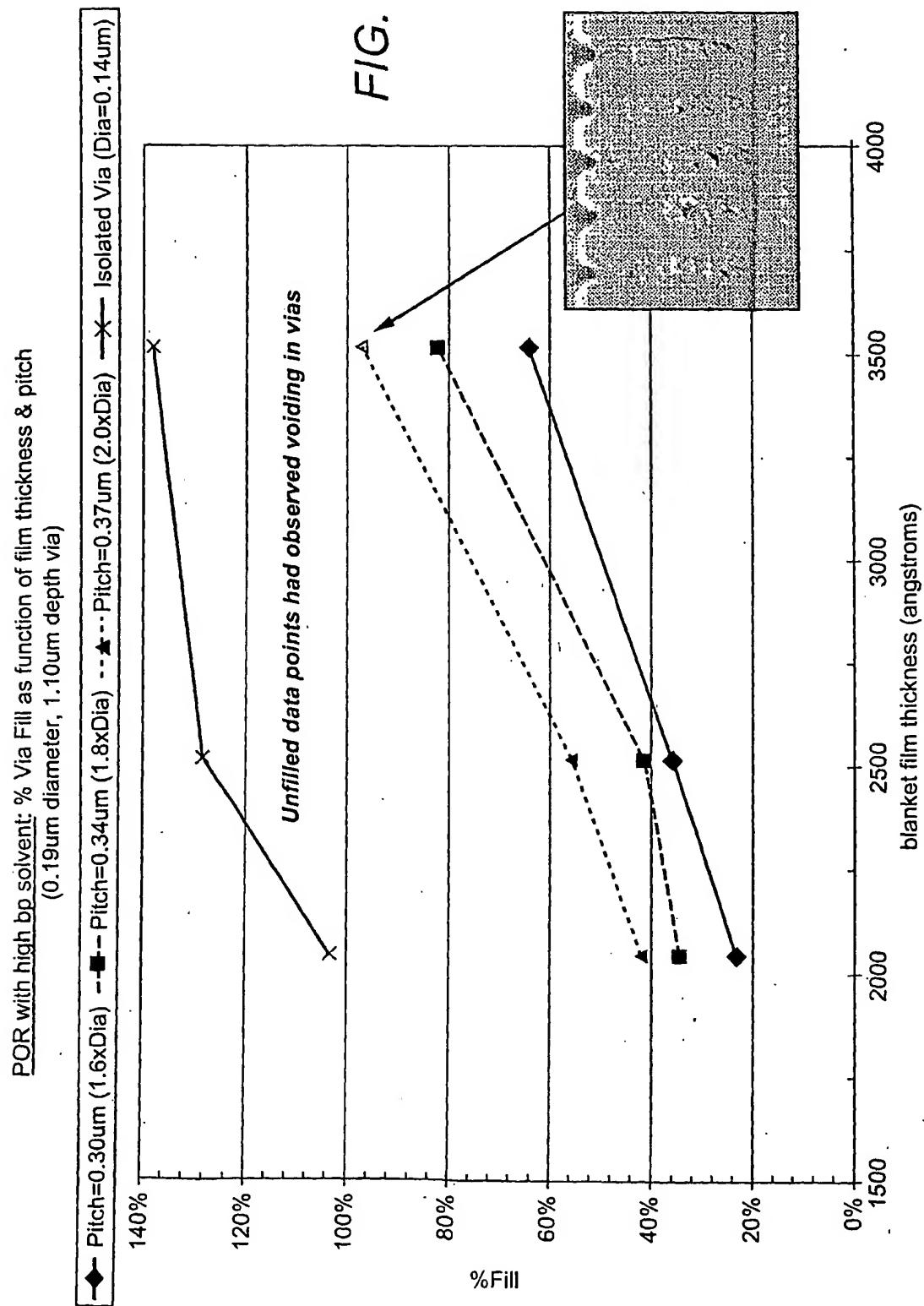
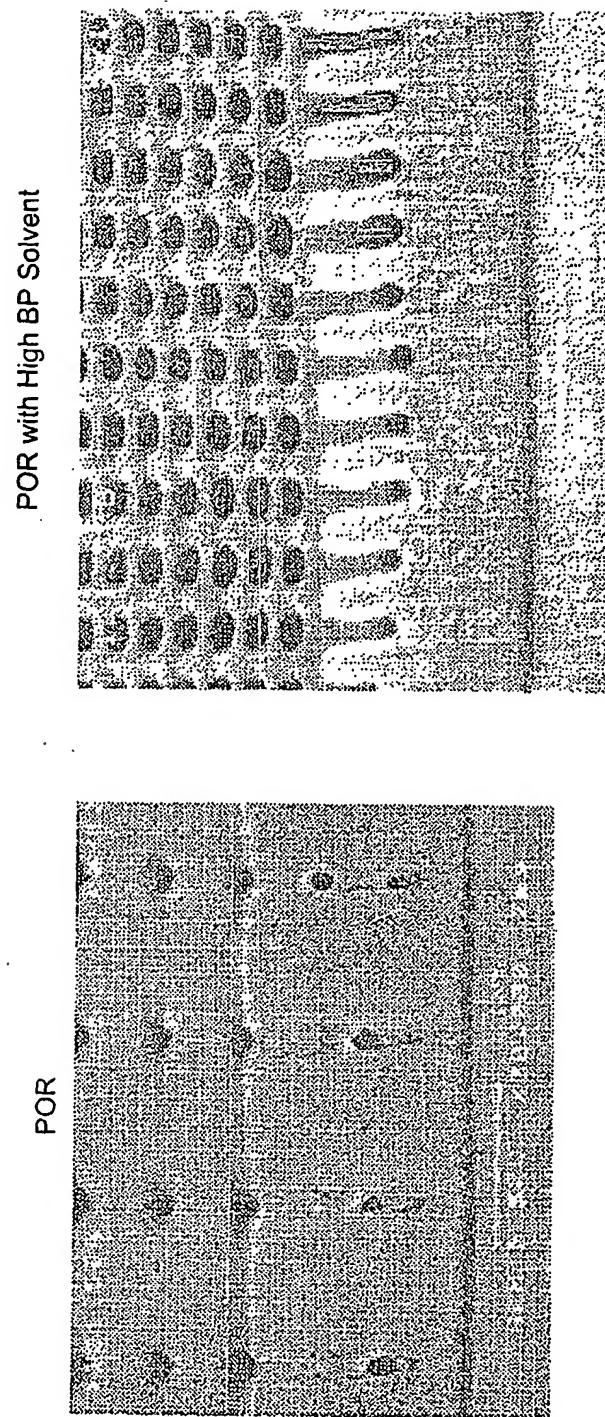


FIG. 28



Via Fill: Addition of High BP Solvent

FIG. 29

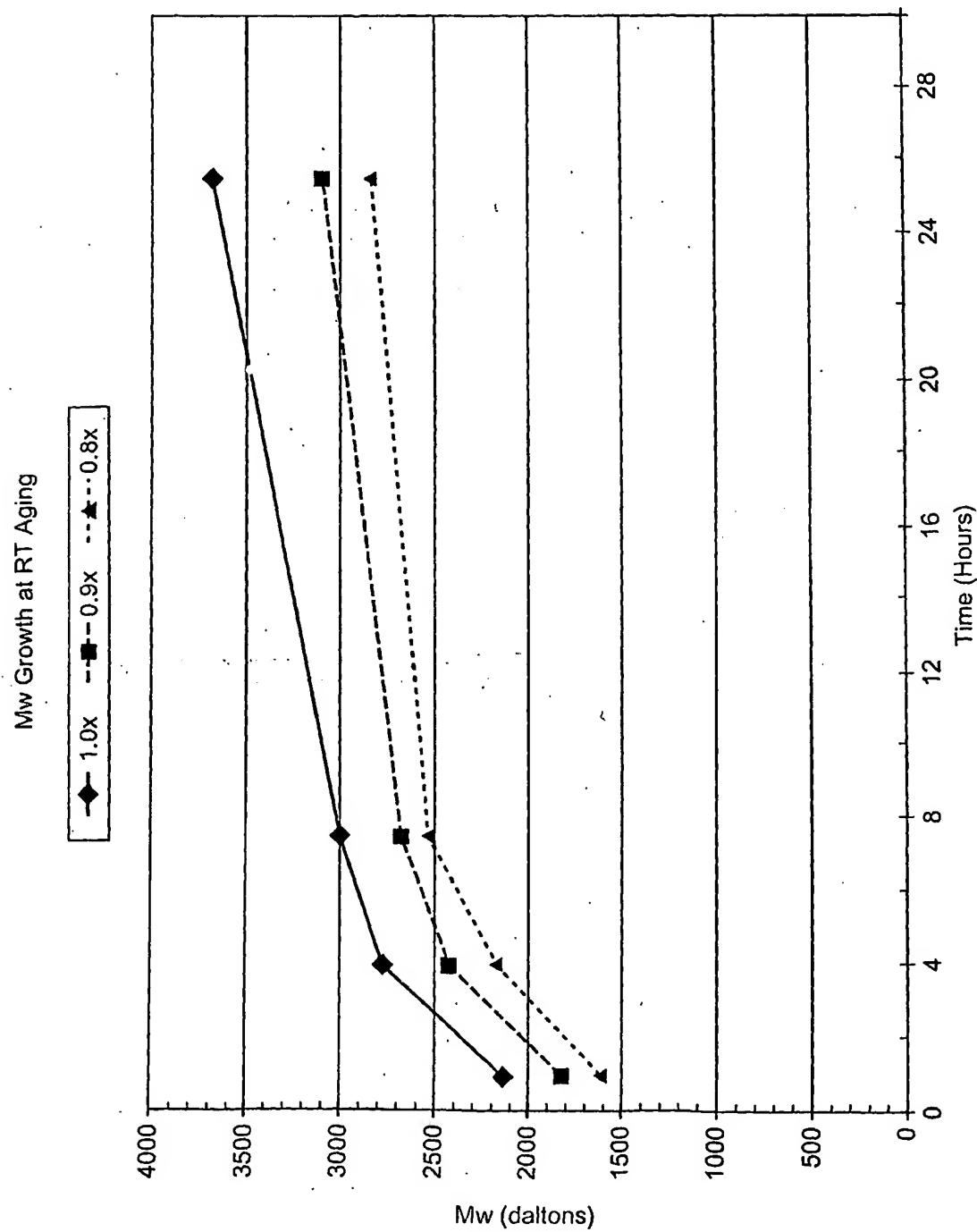
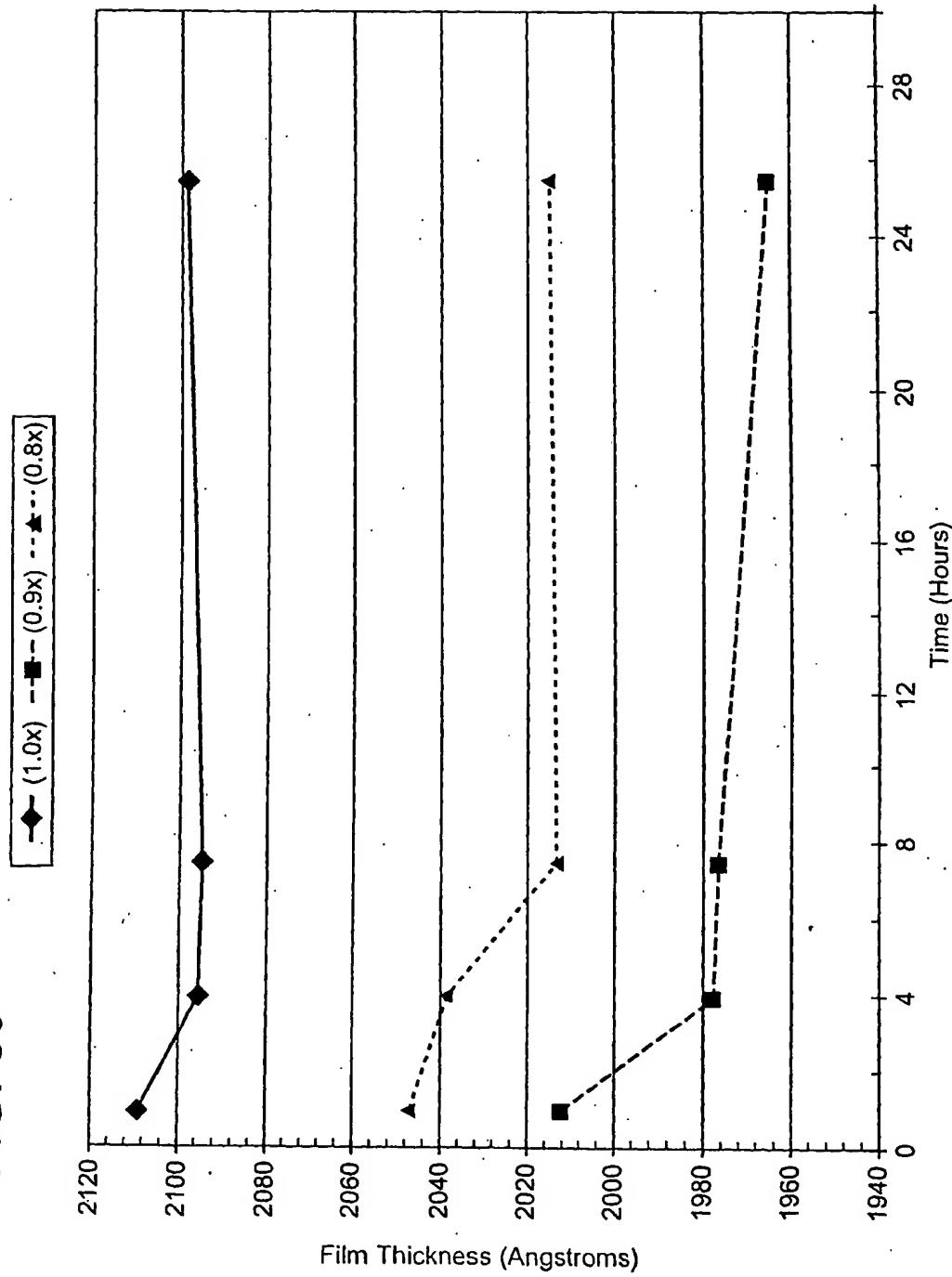


FIG. 30



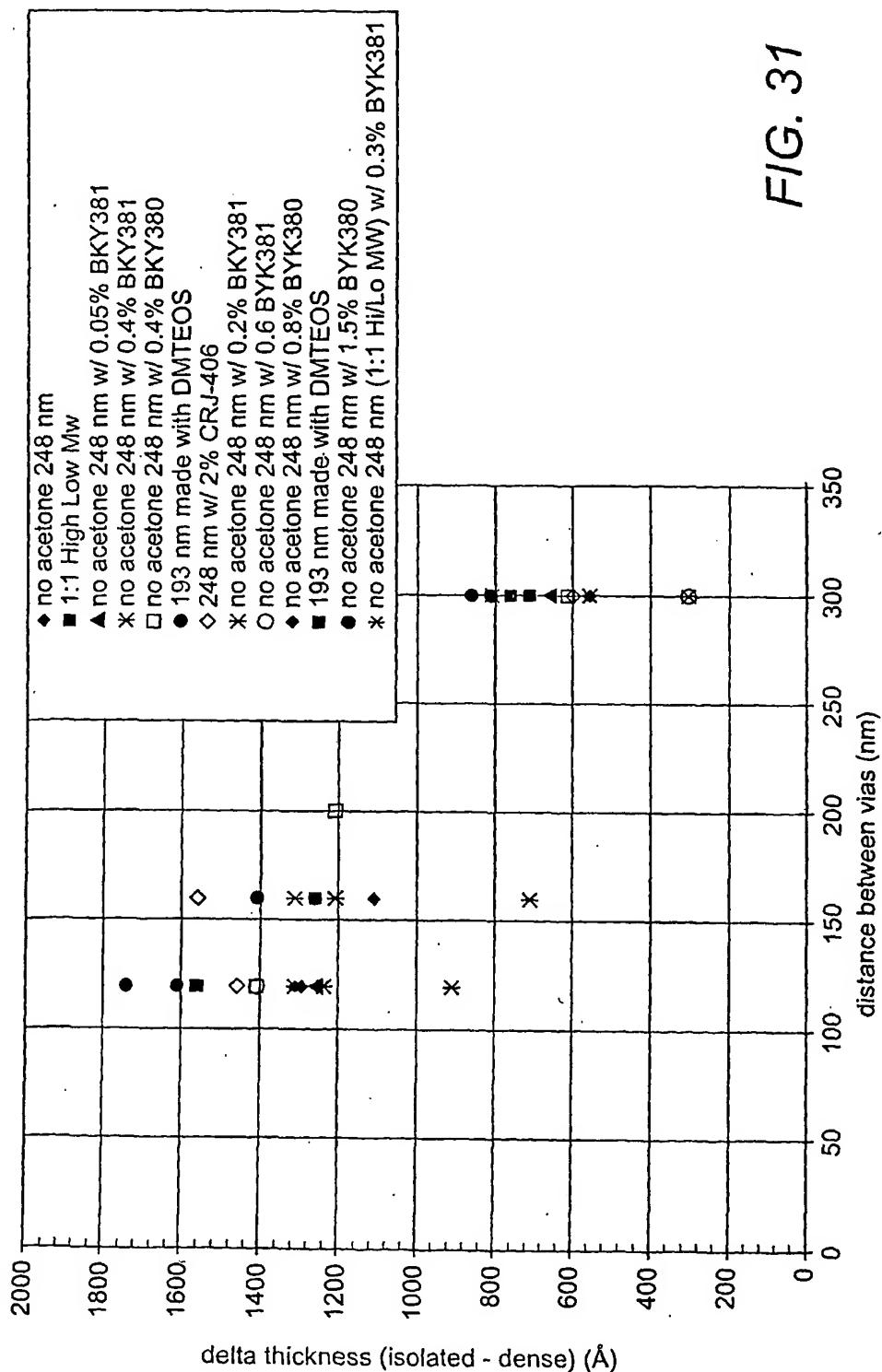


FIG. 31

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C08L 83/06, C08G 77/02, 77/18

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(74) Agent: THOMPSON, Sandra; Bingham McCutchen
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(22) International Filing Date:
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IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT,
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NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility
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ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE,
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Published:

— with international search report

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(88) Date of publication of the international search report:
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For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

WO 2004/044025 A3

(54) Title: ANTI-REFLECTIVE COATINGS FOR PHOTOLITHOGRAPHY AND METHODS OF PREPARATION THEREOF

(57) Abstract: Anti-reflective coating materials for ultraviolet photolithography include at least one absorbing compound and at least one material modification agent, such as at least one porogen, at least one high-boiling solvent, at least one densifying agent, at least one capping agent, at least one leveling agent, at least one catalyst, at least one replacement solvent, at least one pH tuning agent, and/or a combination thereof that are incorporated into inorganic-based materials or inorganic compositions and/or compounds. Suitable absorbing compounds are those that absorb around wavelengths such as 365 nm, 248 nm, 193 nm and 157 nm that may be used in photolithography.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/36354

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C09D 183/06; C08L 83/06; C08G 77/02, 77/18

US CL : 528/39, 10, 41, 43; 106/287.13, 287.16, 524/858, 859

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/39, 10, 41, 43; 106/287.13, 287.16, 524/858, 859

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,368,400 A (BALDWIN et al) 09 April 2002 (09.04.2002), see entire document, for instance the bottom of column 5 through column 6.	1-120

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See patent family annex.

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Date of the actual completion of the international search

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(54) Title: ANTI-REFLECTIVE COATINGS FOR PHOTOLITHOGRAPHY AND METHODS OF PREPARATION THEREOF

(57) Abstract: Anti-reflective coating materials for ultraviolet photolithography include at least one absorbing compound and at least one material modification agent, such as at least one porogen, at least one high-boiling solvent, at least one densifying agent, at least one capping agent, at least one leveling agent, at least one catalyst, at least one replacement solvent, at least one pH tuning agent, and/or a combination thereof that are incorporated into inorganic-based materials or inorganic compositions and/or compounds. Suitable absorbing compounds are those that absorb around wavelengths such as 365 nm, 248 nm, 193 nm and 157 nm that may be used in photolithography.

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